

**Unraveling the Effects of Molecular Confinement on the Dynamics in
Polymeric Systems:**

- I. Block Copolymer Architecture**
- II. Nanoporous Silica Membranes**

A Dissertation Presented for the

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DEDICATION

Dedicated to my wife, Emily King Kinsey, for her love and patience; to my parents, Steve & Terri, for encouraging me to explore; to my sister, Ashley, for her guiding example; and to all of my friends, especially the DeSimones and the Tirpaks.

The best thing for being sad...is to learn something. That is the only thing that never fails. You may grow old and trembling in your anatomies, you may lie awake at night listening to the disorder of your veins, you may miss your only love, you may see the world about you devastated by evil lunatics, or know your honor trampled in the sewers of baser minds. There is only one thing for it then---to learn. Learn why the world wags and what wags it. That is the only thing which the mind can never exhaust, never alienate, never be tortured by, never fear or distrust, and never dream of regretting.

Learning is the thing for you. Look at what a lot of things there are to learn—pure science, the only purity there is. You can learn astronomy in a lifetime, natural history in three, literature in six. And then, after you have exhausted a million lifetimes in biology and medicine and theocriticism and geography and history and economics---why, you can start to make a cartwheel out of the appropriate wood, or spend fifty years learning to begin to learn to beat your adversary at fencing. After that you can start again on mathematics, until it is time to learn to plough.

~Merlin

From ***The Once and Future King*** by T. H. White

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ABSTRACT

In this dissertation, broadband dielectric spectroscopy (BDS) is employed as an experimental tool to probe dipolar relaxations in polymeric systems under two types of molecular confinement. First, a series of miktoarm star copolymers are used to explore how branching block copolymer architectures constrain polymer relaxations within self-assembled domains in relation to their linear counterparts. Secondly, the effects of hard spatial confinement on the dynamics of polymer chains and of ions in polymerized ionic liquids (PILs) are studied after infiltration into silica nanochannels. Other techniques such as transmission electron microscopy (TEM), small angle x-ray scattering (SAXS), and Raman spectroscopy are used to determine various structural length-scales and molecular conformations of the molecules in these systems.

The model system of poly(cis-1,4-isoprene) (PI) is employed to probe polymer chain dynamics by BDS under both types of confinement. Changes in the local and cooperative dynamics compared to those of the bulk PI homopolymer are used to identify how the motions of the chains are altered by environmental constraints. Additionally, within silica nanochannels, surface chemistry modifications are used to study electrostatic interactions between ions and the substrate in hard spatial confinement of PILs. It is determined that an asymmetrical molecular architecture of the miktoarm star copolymer is more influential on the PI chain dynamics compared to symmetric architectures and reduces thermodynamic constraints on the motion of individual blocks. Conversely, for the ABC miktoarm star terpolymer the unidimensional domain interface increases the constraints on PI chains restricting chain motion. Results also show altered dynamics under nanoporous confinement for PI and PILs, namely slower PI chain relaxations and enhanced PIL ionic conductivity compared to similar materials in bulk. These dynamical changes for confined polymeric systems are discussed in correlation to macroscopic properties that are important for materials science applications.

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INTRODUCTION AND OUTLINE

Introduction

The overall focus of this dissertation involves measuring and understanding the molecular motions of polymers and the internal and external forces that contribute to these motions, specifically for polymers under confinement. When some force is included in the description of molecular motion, it is then considered a dynamic motion, or simply dynamics. Understandably, one may view "confinement" as a broadly definable term in the scope of polymer dynamics. However, confinement is simply some restriction of space, quantity, or time. Using this definition, the dynamics under some confinements have actually been considered by physicists for hundreds of years. Unrestricted and random molecular dynamics are most simply described by Brownian motion, which was observed and described in 60 B.C. in Lucretius's Epicurean poem *On the Nature of Things* as spontaneous collisions of particles or atoms, "so the movement mounts up from the atoms and gradually emerges to the level of our senses so that those bodies are in motion that we see in sunbeams, moved by blows that remain invisible".[1] In the advent of Fraunhofer's early 1800's adsorption line experiments, spectroscopic techniques became a reality allowing these molecular motions at particular timescales to be measured.[2] The mathematical derivations of this non-confined random motion was achieved some 100 years later at the turn of the 20th century by Paul Langevin[3]. Finally, in the mid 1900's the physics of polymer motion were developed by researchers like Staudinger, Flory, De Gennes, Rouse, Zimm, Doi and Edwards who expanded the mathematical equations derived by Langevin and the countless experiments that focused on the properties of macromolecular systems.[4-16] Since, the understanding of polymer dynamics have included all sorts of confinements that affect their dynamics.

The results of these chemists', physicists' and mathematicians' works revealed that the motion of polymers is quite different than other molecular

systems and give rise to a plethora of material properties for bulk polymers (e.g. solvent free). For example, restrictions on the random motions of macromolecules can arise just by increasing number of repeat units in a polymer chain, or rather the restriction of quantity. This type of confinement allows polymer materials to stretch and reform their shape following deformation. The polymer dynamics associated with this stretching which deviate from unrestricted, random motions, can be detected by spectroscopic techniques and give rise to elastic material properties. This restriction of quantity was added to Langevin's equations as forces which alter the unconfined motion of the polymer chains.[17] Examples of these forces that confined a polymer's motion include chemical interactions, like electrostatics or hydrogen bonding, or even physical, topological interactions which are termed entanglement. On the other hand, restrictions of space are considered when a molecule exists in a region where the degrees of freedom are reduced in any particular direction. These confinements, introduced mathematically as entropic forces, are included in the understanding of virtually all studies of molecular dynamics, not just polymer dynamics. However, the scope of material properties that arise from these confinements is much more extensive, and in many cases, much less understood for polymers than for other molecular systems.

Polymer confinement, in contrast to similar restrictions of space, quantity or time for other molecular systems, are considered in this dissertation as restrictions to molecular motion that are unique to polymeric systems. For example, the visco-elastic effect for small molecule systems is understood in terms of inter-molecular interactions (electrostatics or hydrogen bonding) which cause individual molecules to associate to form relatively large length-scale multi-molecule chains. While this restriction may occur in polymer systems, there are additional physical entanglements for polymers that exist at much longer time- and length-scales compared to the inter-molecular interactions between small molecules. For a polymer, the lifetime of the covalent bonds that exist between the repeat units

within a chain are virtually infinite compared to the motion of the repeat units themselves, whereas for small molecule systems the repeat units break and reform continuously. The long chains of covalently bonded units result in a unique type of confinement that is present when considering the Brownian motion of polymer systems and is considered in the Rouse model of polymer dynamics. This dissertation describes the changes in dynamics due to additional restrictions to the timescales, length-scales or degrees of motional freedom of polymers. Two particular confinements are considered, and each can be classified as a combination of restrictions to space and quantity which in turn restrict the time associated with the polymer motion. The first confinement type considers the polymers' molecular architecture or branching of polymer chains. The second considers the confinement of polymer chains within extremely narrow cylinders, or nanopores. Additional contributions are examined when charged repeat units, or ions, are present in the polymer chain, and how these confinements affect the transport properties of counter ions are also discussed in relation to the dynamics of the polymer. These two confinements, molecular architecture and within nanopores, are separated in this dissertation, but are both important contributors to the fluctuating dynamics of polymers and to our overall understanding of polymer physics.

Outline

The following paragraphs give an outline of the chapters in this dissertation. The first chapter contains four sections that introduce the chemistry of polymers, dynamical phenomena and material properties that arise from these dynamics, the fundamental theory of polymer chain dynamics, and finally the use of dielectric spectroscopy to measure these dynamics. Then there will be a chapter on the experimental techniques that were used to probe relaxation timescales, self-assembled structures and molecular conformations of the materials under study in this dissertation. The experimental case studies that this dissertation uses to

understand how confinement can alter the dynamics of polymers are then presented. These case studies are divided into two parts: Part I (Chapters 3-6) focuses on the role of molecular architecture on polymer dynamics within self-assembled block copolymer domains; Part II (Chapters 7 and 8) explores how polymer and ion dynamics are affected by confinement within nanometer sized silica pores. The final section of this dissertation gathers the individual results from each study into an overall conclusion for polymer dynamics under confinement.

The first section of Chapter 1 introduces the chemistry of long chain molecules. The second section describes how the orientations of polymer chains in space and the dynamics of the chain give rise to their unique mechanical properties. The third section covers the mathematical foundations of normal modes and cooperative motion, then contextualizes this motion within the Rouse theory of polymer dynamics. This theory is expanded beyond the dynamics of the Rouse chain to tie in chain conformations and topological polymer entanglements which predict their mechanical properties. Finally, the fourth section of Chapter 1 connects the polymer dynamics theory with the relaxations measured by dielectric experiments with a focus on poly(*cis*-1,4-isoprene) homopolymer chains from the literature. The experimental details for dielectric measurements, which are the basis for evaluating chain dynamics in the case studies of this dissertation, are comprehensively summarized in Chapter 2 along with the other experimental techniques used in this study. Chapter 2 will primarily focus on broadband dielectric spectroscopy (BDS) and connect the normal mode theory from Chapter 1 with the dielectric theory for measuring the dynamics of polymeric systems.

Part I covers the experimental perturbation of dynamics in block copolymer systems with star branched architecture, with a detailed introduction in Chapter 3 that covers the theory of phase separation and a meta-analysis of the relaxations of poly(*cis*-1,4-isoprene) in linear diblock copolymers from the literature. Next, Chapter 4 compares the relaxations of poly(*cis*-1,4-isoprene) in linear diblock copolymers with the highly polar poly(2-vinylpyridine) counter block to determine if

the coincidence of dielectric relaxations at similar timescales and temperatures for the glassy block influences the dynamics of the poly(cis-1,4-isoprene) chains. Chapters 5 and 6 employ seven miktoarm star copolymers with polystyrene and poly(cis-1,4-isoprene) blocks with symmetric or asymmetric architectures. Chapter 5 focuses on the dynamics in the architecturally symmetric 4-arm and asymmetric 3-arm miktoarm star copolymer systems that self-assemble into lamellar morphologies and compares the dynamics to that for linear diblock copolymers. Finally, Chapter 6 expands on the findings from Chapter 5 to cover other morphologies and further examines the effect of the asymmetric chain architecture in a more complex miktoarm star copolymer. Chapter 6 also presents the findings on the effect of poly(cis-1,4-isoprene) molecular weight on the chain dynamics for the 3-arm miktoarm star copolymers.

In Part II, the dynamics of polymeric systems are investigated under hard spatial confinement within nanoporous silica membranes and separated into two chapters that are preceded by an introduction covering the state of the nanoporous media field. In Chapter 7 the dynamics of polyisoprene chains with increasing chain size approaching the size of the confining 7nm diameter pores. Chapter 8 revisits the ion dynamics in PILs which are synthesized *in situ* within silica nanopores. Chapter 8 also considers the effects of different pore surface interactions on the properties of the synthesized PILs.

The final section of this dissertation will summarize the major conclusions of these investigations on molecular confinement of polymer systems and connect them with engineering applications. These applications will be considered within the context of the direction of future research in the field.

Chapter 1: Theoretical foundations for polymer dynamics

The primary building block of the physical, material universe we exist in is the atom. Toward smaller length-scales and described by models based on quantum theories, each atom is defined by the number of protons and neutrons in its nucleus and the number of electrons surrounding that nucleus. Toward larger length-scales interactions among these constituents allow atoms to join together to form molecules. Nearly everything that we can see and touch every day is made of molecules that are comprised in some virtually infinite number of combinations of atoms that follow a strict set of physical laws. How the relative charges of one molecule interact with those in a neighboring molecule and how these interactions contribute to useful physical properties is the basis of materials science. The chemical physics that govern the behavior of simple molecules to molecules with thousands of atoms, or macromolecules, are the same, but are implemented at different length- and time- scales. The physics that govern the behavior of biological macromolecules such as DNA and proteins and the behavior of synthetic polymers all stem from the interaction of one molecule with its surroundings. The field of polymer physics includes theories developed to describe the dynamics of polymers and to predict their properties. A thorough understanding of these theories is required to follow the studies in this dissertation.

This chapter will detail the chemistry and physics of polymers. Here, several decades of experiments and theory will be summarized to uncover the current state of knowledge of polymer dynamics and how these dynamics govern the properties of polymeric systems. The relatively simple theory of linear polymer chains in this chapter will be the basis for Parts I and II. Then, in Part I and II, the theories described in this chapter will be expanded upon for the more complex dynamics of confined polymer chains in block copolymer systems with non-linear architectures and for confined chains in nanoporous channels, and how these confinements cause deviations from the dynamics described here. The first section of this chapter covers synthetic techniques and the chemistry of polymers and the

statistical basis of a chain. The next section covers the physical properties that result from the dynamics at different timescales and temperatures, like the physics of glasses and viscoelasticity. Next, the particular models that are used to describe these physical properties in terms of dynamics of the polymers including Rouse theory and the statistical thermodynamics of the Gaussian chain. Then, the effect of ions and the corresponding transport properties will be described for polymeric systems as these aspects are also examined for each type of confinement that is studied in this dissertation. Finally, a brief introduction into the certain confinements that are considered experimentally in this dissertation will be laid out within the scope of the dynamics described above, as well as an introduction into the dipolar motions of polymers and how they are utilized in experiments to measure their motion.

Chemical Structure and Chain Topology

Polymers are long chain molecules made up of repeating units or segments. For biological polymers such as DNA, there are five types of repeating units called nucleic acid, or such as proteins, where there are twenty-one types of repeating units called amino acids, or for starches which are polymers made up of various types of sugar repeat units. The simplest types of polymers, homopolymers, contain only a single type of repeat unit, and many homopolymers exist through man-made synthetic routes. Although synthetic homopolymers, colloquially known as plastics, are simple, their macroscopic properties can be specifically tuned based on how the molecular chains interact with each other and how they collectively move. However, before delving into the properties and dynamics of polymers, first it is important to understand the basic chemistry of polymers. That is, what are the different types of repeat units that make them up, the various techniques that are used to produce them, how to control the number of repeat units in the chain, how multiple homopolymers may be combined into a single heteropolymer chain, and how controlling this connectivity can alter the behavior

of a blend of the homopolymers. By using these molecular handles to prepare a virtually endless number of polymer types, there is similarly a continuous range of properties that can be realized by systematic design that is based on the chemical make-up of the chains, their connectivity and how these chains move.

The first semi-synthetic polymers were made by Charles Goodyear in the mid 1800's by cross-linking natural rubber, a bio-homopolymer called poly(*cis*-1,4-isoprene), with sulfur through a process called vulcanization as shown in Figure 1. Nearly sixty years later, the first fully synthetic, commercially available polymer was made by Leo Baekeland by mixing the reactant phenol with formaldehyde in the presence of an acid. The reaction in Figure 2 shows the mechanism where the repeat unit A is formed, then subsequently reacts with remaining reactants to produce the branching polymer chain. Bakelite, rather than forming cross-links of linear chains like for vulcanization of polyisoprene, is highly branched but also a highly cross-linked polymer network. The chemical structures of vulcanized rubber and Bakelite were not realized until Hermann Staudinger demonstrated that they were indeed long chain molecules made of many hundreds of short, covalently linked repeat units. The competing theory of the time was that these materials were made of aggregating colloids that caused the measured mass of a single molecule to be artificially large. However, Staudinger, the first scientist to use the term "macromolecule", proved to be correct, and thus began the growth of the polymer chemistry field. There are two primary types of polymerization reaction mechanisms in polymer chemistry: step growth and chain growth. The difference between the two is how the repeat units are added to the growing polymer chain. In step growth, monomers react together to form multiple growing chains, and subsequently these chains and/or other monomers can link together to continue the growth of the chains. In chain growth, only one unit at a time is added to the chain, therefore, extending its length by sequential monomer addition at the end of the growing chain.

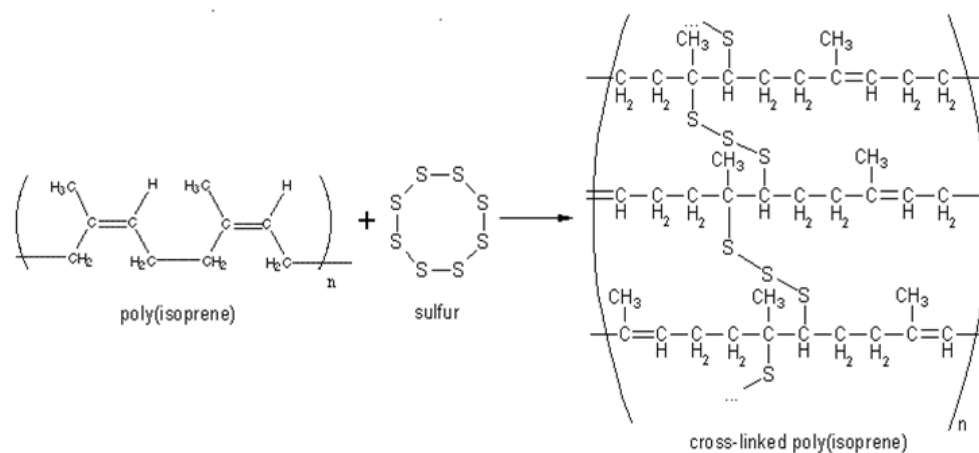


Figure 1: Generalized vulcanization reaction of poly(cis-1,4-isoprene) to form cross-linked natural rubber. Reproduced from Quora.com.

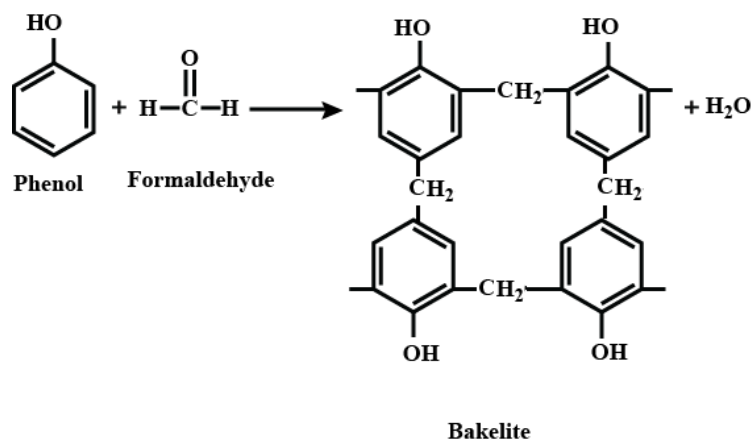


Figure 2: Simplistic reaction mechanism of polymerization for cross-linked Bakelite. Reproduced from Quora.com

The most common chain growth technique, free radical polymerization, is shown in Figure 3. This involves an initiator that splits to form highly reactive radical species that begins polymerization, the chain extends by propagation where the radical electron is transferred to the end of the growing chain with the addition of each monomer, and finally the radical is quenched by termination. The size of the chains in the reaction can be controlled by certain chain growth reaction conditions that slow down the reaction kinetics and limit the mechanism of termination. There are two techniques that will be the main focus for controlling polymer size by chain growth mechanisms in this dissertation, and they are reversible addition-fragmentation chain-transfer (RAFT) polymerization and anionic polymerization.

The polymers prepared in Part I of this dissertation were prepared by anionic polymerization while the majority of the polymers in part II were prepared by basic free radical polymerization or RAFT polymerization. Anionic and RAFT polymerizations are considered living polymerization reactions where termination is virtually removed from the steps in Figure 3. RAFT polymerization follows the conventional free radical polymerization which includes the initiator, monomer and solvent. However, it also requires an additional molecule, called a chain-transfer agent, which stabilizes the radical on the growing chain ends in equilibrium with the chain-transfer agent molecule. For anionic polymerization, a highly reactive organolithium species, often *sec*-butyllithium, forms a cation that stabilizes the reactive anionic growing chain end. The removal of the termination step in each of these techniques requires that no reactive impurities, such as water or oxygen, are present. The controlled introduction of such an impurity to the reaction is used to complete the reaction but is detrimental to the reaction during the propagation stage. Ideally for these techniques, all of the polymer chains contain the same number of repeat units and this number can be controlled and predicted by specific reagent concentrations and reaction conditions.

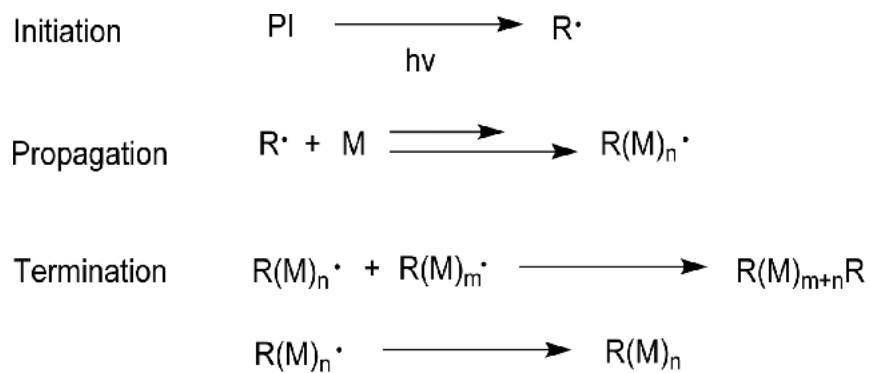


Figure 3: The reaction mechanism for free radical polymerization. PI is photoinitiator, R is a radical initiator, M is a monomer. Two termination steps are possible. The first is combination, where two propagating chains react to form a single chain. Typically, the more desired second termination mechanism is achieved by quenching the reaction with air or solvent. Reproduced from [18].

The number of repeat units (i.e. degree of polymerization) and the distribution of molecular weights present in a polymer sample can vary the dynamics and properties of the system, as will be discussed later in this chapter. Therefore, knowing the distribution of chains sizes in a polymer sample is essential to isolate the effect of chain length on the material properties. The more intuitive way to determine the molecular weights in a polymer sample is the number-average molecular weight (M_n). The M_n uses the typical molecular weight definition where the molecular weights of all of the chains in a sample ($W = \sum_i n_i w_i$, where n is the number of "i" chains with molecular weight w_i) is divided by the total number of polymer molecules in the sample ($N = \sum n_j$). Alternatively, the weight-average molecular weight (M_w) of a polymer sample accounts for the fact that chains with more monomers account for a larger percentage of the overall weight of the sample (i.e. a weighted average). These are shown in Eqn. 1. If all the chains in a sample are the same size, then the M_w and M_n are the same and there is no distribution in molecular weights. However, when there are chains of different sizes, the M_w will be greater than M_n . The quotient of M_w and M_n gives an index of the dispersion of molecular weights in a sample, and is termed the polydispersity index (PDI) or simply dispersity in Eqn. 2.

$$M_n = \sum_i [n_i w_i (n_i)^{-1}]; M_w = \sum_i [n_i w_i^2 (n_i w_i)^{-1}] \quad 1$$

$$PDI = M_w / M_n \quad 2$$

Polymers with all of the repeat units (typically with > 20 monomers) of the same molecular structure are called homopolymers. These are the simplest types of polymers, but have unique properties compared to other chemical materials. Oligomers, or molecular chains of <20 monomers are important chemical tools that are used to understand the differences between low molecular weight molecules and polymers. However, many of the properties that are unique to polymeric systems are governed by the high molecular weight. Also, different monomer types

give rise to different properties, which are typically understood in terms of the flexibility of the backbone due to hindered rotation from the side group and the interactions of these side groups in neighboring units and neighboring chains. More details about these properties are discussed in subsequent sections of this chapter.

During the polymerization reaction, some monomers may be subject to different reaction mechanisms as they are added to the growing chain end. Even if all of the monomers are the same, the differing mechanisms can result in inhomogeneities of the repeat units within the chain. For example, Figure 4 shows different chain growth mechanisms for two different polymers. First polyisoprene is shown where the monomer reacts at a different carbon within the chemical structure of the monomer. This causes the chemical structure within the polymer backbone to be slightly different than the one before it. This same chemical make-up that is slightly different due to the connectivity or configuration of atoms is called isomerism, and when it is controlled during polymerization, can ultimately yield different properties of the final material. The second example is another model polymer called polystyrene. The benzene ring off of the backbone of a polystyrene molecule can take two different configurations, or react head-head, tail-tail or head to tail. While some reactions are more preferential, this does not mean the other possibilities do not take place. Among the different configurations possible for the addition of repeat units, if all of the monomers add in the same way the final structure and behavior will be different than if the alternated. This is called tacticity, where an isotactic polymer has repeat units of all the same configuration, a syndiotactic polymer has monomer configurations that alternate, and atactic is where there is no order associated with the configuration of repeat units. Another topic that is considered within this context is chirality, where different isomers are connected in the same way but their relative order or rotation about a central point differs. Also, in Figure 4 is an example of chirality, but not configurational chirality.

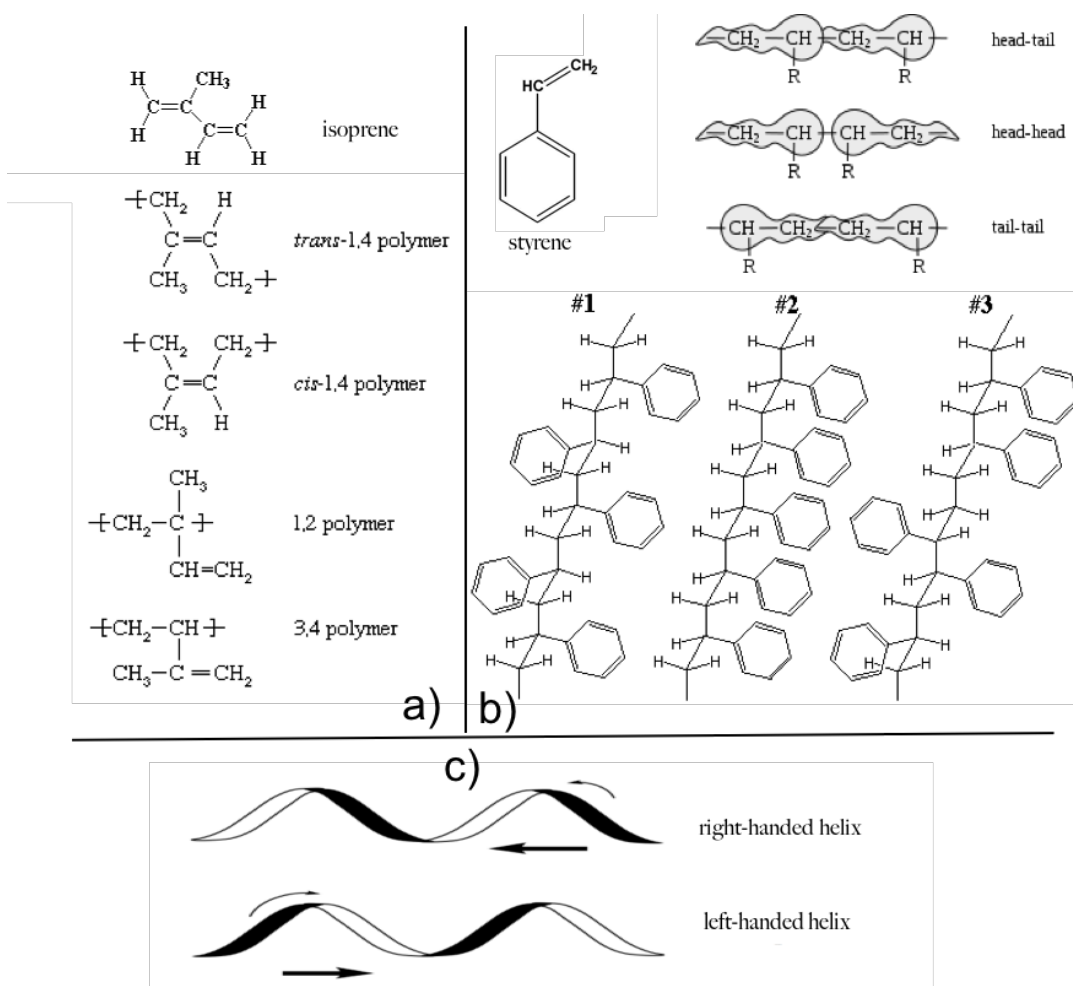


Figure 4: Isomeric systems of polyisoprene (a, used from Britannica), polystyrene with differing tail/head linkages as well as examples for isotactic #1, syndiotactic #2 and atactic #3 configurations (b, used from stanford.edu) and examples of conformational isomerism with respect to chain twisting (c, used from C. Schaller, St. John's University).

The conformational chirality example shown in Figure 4c is of particular importance for biopolymers such as a protein or deoxyribonucleic acid (DNA). The conformation of a polymer chain is a description of how the chain as a whole bends and adapts to form a certain physical structure in space. When there is a specific structure for this conformation, chirality can be included in this description. For example, DNA molecules are found to have a right-handed helical twist as opposed to a left-handed twist and thus, DNA has chirality in the helical chain conformation.

While these biopolymers are great examples of conformational chirality, this is rarely observed in homopolymers. There are five different monomeric units in a DNA molecule that govern its the conformation of the polymer, and 21 different monomers that make up most proteins. Polymers with two or more types of monomers are called hetero- or co-polymers. The order of the monomers in a copolymer can be random or highly controlled based on the desired chemical structure which extends the various physical or chemical properties possible for polymeric systems beyond the homopolymer. Additional complexity may be introduced into polymeric systems when rather than one long linear chain, there are one or multiple branching points. Often times these branches are chemically connected to form a polymer network, not dissimilar to vulcanized polyisoprene from Figure 1 or Bakelite in Figure 2. Various synthesis methods have been developed to precisely control the addition of monomers, the monomeric isomer that is formed when it is added, the order of multiple monomers and the branching and crosslinks in a polymer material. Further discussion about these methods will be briefly covered in the different parts of this dissertation, but the primary focus is the behavior and motions of the chains and the monomers that form them. Understanding how the different local chemical and physical environments effect the dynamics of these systems is ultimately how engineering and design methods are employed to tune the vast array of material properties that are possible for polymer systems.

The backbone of many polymer systems are formed by some number “ n ” of simple carbon-carbon linkages (*i.e.* polyethylene). The length of a vector formed by this linkage is on the length-scale of $l \sim 1.5 \text{ \AA}$. Due to the electronic structure and hydrogen atoms of each carbon, the angle between the bonds at the node of a single carbon atom is typically held at $\theta \sim 68^\circ$. However, the torsional rotation about a carbon atom node begins to influence the conformation of the polymer chain. In Figure 5a polyethylene backbone is shown with each carbon numbered along with the angles among them. As the torsional angle ψ changes, bends or kinks in the backbone are formed. This rotation typically occurs with some energy cost due to steric hindrance, or physical and chemical interactions of monomeric side groups. The bottom panel in Figure 5 shows a schematic of the energy cost of rotation about ψ . If all of the bonds in a polyethylene chain are considered, the maximum possible conformational length ($R_{\max}$) of the chain where all $\psi = 0^\circ$ can be calculated by

$$R_{\max} = nl \cos \theta \quad 3$$

The simplest model to mathematically describe a polymer chain, called the random walk model, uses the lengths of the bond vectors and bond rotation to quantitatively describe some conformational length-scales of the freely joined chain. This model defines the location of some point along the polymer chain by a vector $\mathbf{r}_i$ which is then separated from $\mathbf{r}_{i+1}$ by the so-called Kuhn length b . Using the random walk, the sum of all jumps of each bond vector over time $\sum_{i=1}^{n-1} (\mathbf{r}_{i+1} - \mathbf{r}_i)$ defines the end to end distance of the chain $\mathbf{R}(n,t)$. Then, maximum equivalent length analogous to Eqn. 3 for the freely joined chain contour is $R_{\max} = nb$, and the mean squared end to end distance over time is

$$\langle \mathbf{R}(n,t)^2 \rangle = nb^2 + \langle \sum_{i \neq j}^{n-1} (\mathbf{r}_{i+1} - \mathbf{r}_i) \cdot (\mathbf{r}_{j+1} - \mathbf{r}_j) \rangle \quad 4$$

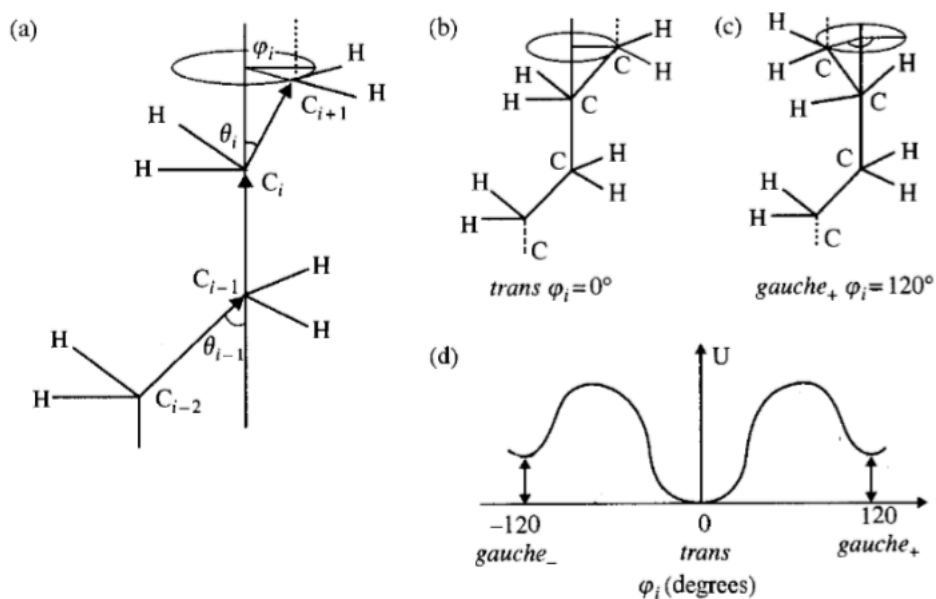


Figure 5: Rotational isomerism of a four-carbon chain with angle between carbons θ and torsional angle of rotation ψ (a). There are two conformations where all four carbons exist in a single plane: when $\psi = 0^\circ$ (*trans*) and when $\psi = \pm 120^\circ$ (*gauche*) (b and c, respectively). The energy associated with this rotation is at a minimum for *trans*, and a local minimum for *gauche* (d). Reproduced from [19] with permission.

Since all bond vectors are randomly oriented, the second term in Eqn. 4 averages out to zero. For the random walk model, each vector does not necessarily represent a bond between carbon atoms, and in a real polymer there is not a free rotation about ψ . For the random walk, Flory used a ratio of $\langle \mathbf{R}(t)^2 \rangle$ to $R_{\max}$ to generally restrict the rotations of a chain with infinite length to more accurately describe the flexibility of real polymers[14]. This ratio is called the characteristic ratio C_n and is defined by the average angle θ between all $\mathbf{r}_i$ and $\mathbf{r}_{i+1}$ using

$$C_n = n^{-1} \sum_{i=1}^n \sum_{j=1}^n \langle \cos \theta_{ij} \rangle \quad 5a$$

$$\lim_{n \rightarrow \infty} C_n = C_\infty = \langle \mathbf{R}(t)^2 \rangle R_{\max}^{-1} \quad 5b$$

Eqns. 5 are then used with Eqn. 3 to define the Kuhn length b of a particular polymer as the hypothetical length of a bond in the freely joined chain that is sufficient to accurately represent the length-scales of the real polymer chain.

$$b = C_\infty n l^2 R_{\max}^{-1} \quad 6$$

In addition to the Kuhn length, another informative lengthscale of the chain is the persistence length $l_p \sim 0.5b$ which defines the distance between segments in a real polymer chain whose motions are completely uncorrelated. These descriptions of segments that make up a freely joined chain and how the motions of these segments relate to one another, are the foundation for understanding polymer dynamics. While the properties of polymers may be modeled relatively well using b , experimental studies have shown they do not accurately describe some real polymer systems in the glassy state [20-22]. Methods used to describe polymer dynamics in a self-consistent way ranging from length-scales of the segment to the chain to have been developed and tested over several decades of scientific research to predict the resulting physical properties of these materials. The next sections will first describe physical properties that are governed by the dynamics of polymer chains in the glassy and rubbery states, and the most basic systems

will be used to depict the cooperative motion of segments within a single chain. Then, the models and statistical methods to mathematically describe these dynamics when restrictions to the freely joined chain are imposed to account for realistic physical constraints will be covered followed by a summary of studies from the literature that measure these dynamics and test the theories.

Dynamical Phenomena and Physical Properties

The physical properties of polymers are ultimately derived from the rates or timescales of their motion at different length-scales. For example, the motions of individual segments of a polymer chain govern the most widely studied dynamical phenomena of modern plastic materials, the dynamic glass transition. This dynamical phenomenon is the gradual slowing down of molecular motion as temperature decreases as is displayed in Figure 6. While polymers are not the only materials whose molecular motion can undergo the dynamic glass transition, they will be the focus of this section. The dynamic glass transition is a second-order thermodynamic transition where the evolution of the glassy state does not occur with an abrupt release or absorption of heat to or from its surrounding and does not coincide with a particular change in molecular density. This is in direct contrast to crystallization at T_m , which is a first order transition from a liquid state to a solid state, where there is an abrupt change in specific volume and/or enthalpy at a particular temperature or pressure resulting in a significant entropic change (*i.e.* molecular order is altered from amorphous to a highly ordered). These transitions are shown in Figure 6a. Many polymers can form a crystal structure, but all polymers form amorphous phases that, upon cooling, become rigid and solid-like because the motion of the polymer segments of is essentially arrested. In this way, the dynamic glass transition is an entropic event that is related to cooperative molecular motion in an amorphous state. The dynamic glass transition has been the topic of many scientific discussions over the past several decades.

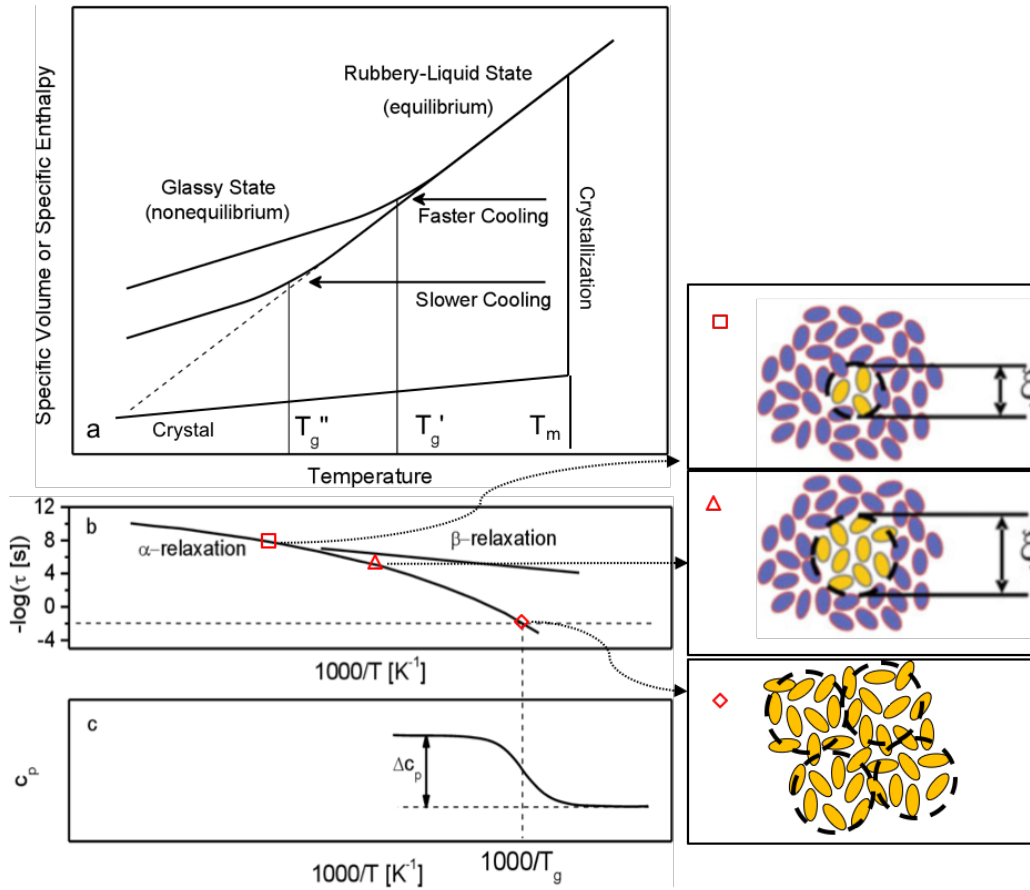


Figure 6: Thermodynamic transitions of crystallization and the dynamic glass transition shown through the temperature dependence of the specific volume and enthalpy (a). The relaxation times associated with the dynamic glass transition approaching the T_g and some relative lengthscale associated with these dynamics (b). Finally, the specific heat capacity change associated with the calorimetric glass transition temperature (c). The lengthscale sketches on the right are adapted from [23] and plots b and c are adapted from [24].

One of the most prominent models that describe the dynamic glass transition is the Adam-Gibbs model which employs a thermodynamic balance between temperature and entropy through cooperative motion of molecules within a particular, temperature-dependent volume (ξ^3). This is schematically shown in Figure 6b along with the characteristic rates (τ_α) of the coordinated motions of the species within ξ^3 at a particular temperature (see red square, triangle and diamond in Fig. 6). At $T=T_g$, there is no abrupt change in specific volume but there is a heat capacity change (ΔC_p) as displayed in Figure 6c. The thermal conformational entropy S_c associated with this transition in cooperative motion by the Adam-Gibbs model follows

$$S_c(T) = \int_{T_0}^T \Delta C_p T^{-1} dT \quad 7$$

The temperature at which $\tau_\alpha = 100$ s is denoted the calorimetric glass transition temperature (T_g). For polymers it has been determined experimentally and through simulations that the cooperative motions of the T_g is associated with a volume containing ~ 3 Kuhn segments. However, when the local environment of these coordinated motions may be altered due to some confinement (spatial, temporal, etc.) which then effects the length-scale of ξ , ultimately affecting T_g . This was shown by the Adam-Gibbs model through S_c by assuming the heat capacity takes the form $\Delta C_p = D T^{-1}$ [25]. In this case S_c in Eqn. 7 becomes negligible as $T \rightarrow T_0$. From this assumption for ΔC_p , it was shown that ξ has a temperature dependence of $\xi \sim (T-T_0)^{-2/3}$ [26]. Then, as mentioned, when the local environment of the polymer is altered, the behavior of these cooperative motions are also altered due to changes in the free volume.

The correlations of these motions ultimately contribute to the autocorrelation function of the material ($\Phi(t)$) in response to an external force $f(t)$ that perturbs the molecules out of equilibrium for some amount of time t . Then when $f(t)$ is removed the displaced molecules “relax” back to equilibrium. The autocorrelation function will be described in more detail later. For now, it should be

noted that the dynamics are measured by relaxations of the molecules in the material at different timescales and temperatures in response to an external force. For example, while the T_g is defined as the temperature for the cooperative motion of molecules within a particular volume at $\tau_\alpha = 100$ s, but the T_g is measured by perturbing the system from equilibrium for some amount of time, the measuring the time it takes for the system to return to equilibrium. The relaxation of the T_g are termed structural relaxations as the prominent structural integrity of the material changes for a glass at this temperature. Understanding the physical, dynamical properties of polymers are discussed here within the context of molecular relaxations which ultimately determine useful material properties. Such relaxations occurring in response to an external shearing force σ after mechanical deformation or strain γ is shown in Figure 7. over time (top) and temperature (bottom) for some representative polymer material. The linear response of this material to mechanical deformation is given by the Maxwell relation where $G(t)$ is the modulus

$$\sigma = G(t) \gamma \quad 8$$

When the time to return to equilibrium is 100 s and occurs at the length-scales of ξ at a particular temperature, that temperature is the T_g . The modulus at T_g and τ_α defined as the structural relaxation is where the polymer begins to flow and is defined with the viscosity η and instantaneous shear modulus G_∞ by

$$\eta = G_\infty \tau_\alpha \quad 9$$

At temperatures above T_g the material will flow and/or have elastic properties; at temperatures below T_g the material will behave like a solid as denoted in Figure 7.

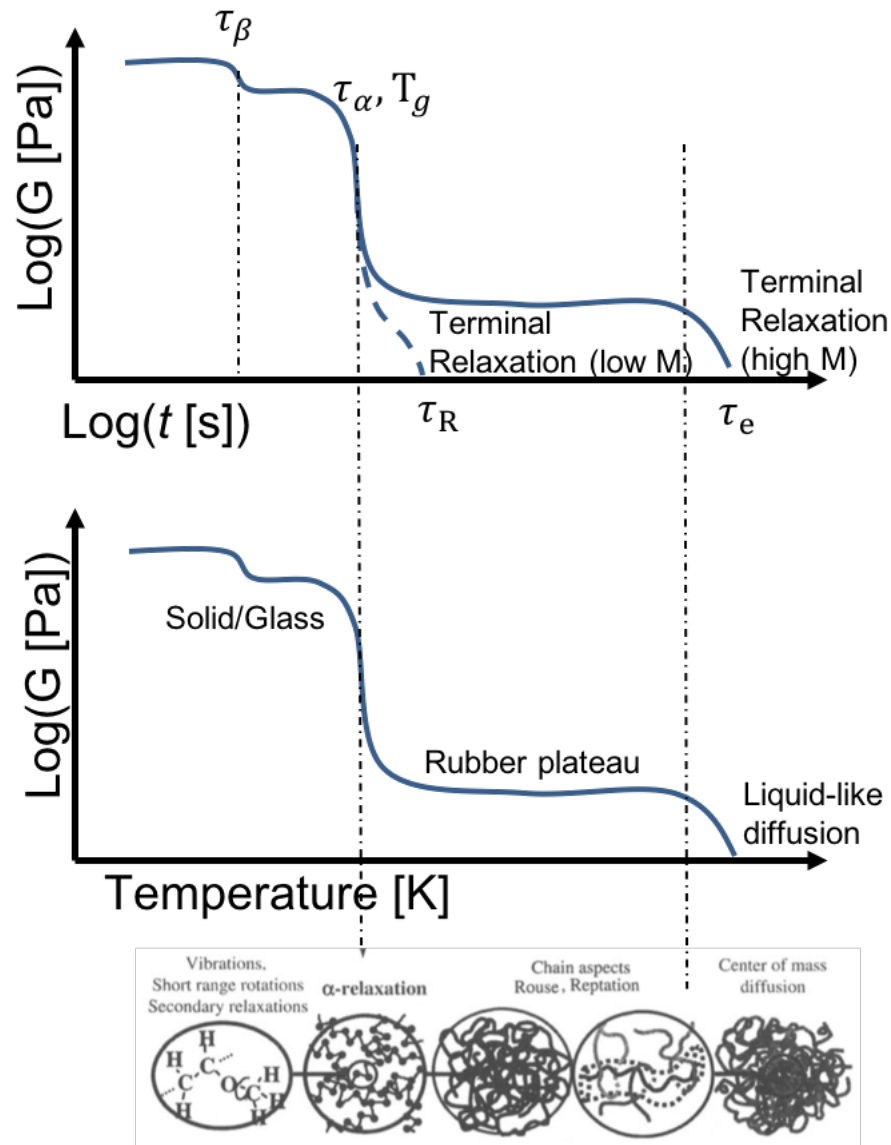


Figure 7: The mechanical shear modulus $G(t)$ plotted vs time where characteristic relaxation times τ are identified (top) and vs temperature where the property of the material is identified (bottom). Below these plots sketches that represent the lengthscale of the secondary relaxation, structural relaxation, chain relaxation, and terminal relaxations are shown. The sketches are reproduced from [27] with permission.

At polymer lengthscales above and below that for individual segments associated with the T_g , there can be more localized motions of monomeric side groups as well as motions of the entire chain as it interacts with other neighboring chains, respectively. In the amorphous solid state, localized motions below the lengthscales that govern flow are still possible. These dynamics are termed Johari-Goldstein (JG) relaxations in which side groups of the polymer fluctuate within a “cage” formed by the polymer segments. For simulations of molecular liquids, these cage-dynamics have been shown to be isolated throughout the system, whereas in polymers if any local orientations exist, then effectively all of them do [28]. As the temperature increases beyond T_g , the cages of polymer segments and the JG relaxations amalgamate with the dynamics of the structural relaxation. In other words, the localized side group motions, while occurring at a different length-scale, become virtually indistinguishable from the motions of the polymer segments. The JG relaxation is also called secondary, or β -relaxations, as shown in Figure 7 and in the timescales in Figure 6b.

For $t = \tau_\alpha$ the polymer material displays viscoelastic properties as defined by Eqn 9. For a liquid-like polymer at much longer times than τ_α , η describes this behavior. At shorter times, closer to τ_α , the elasticity of the material is described by G_∞ . This is shown for a viscoelastic liquid using the Maxwell model in Figure 8a where the dashpot is described as an incompressible Newtonian fluid at long times which follows $\sigma = \eta \, dy/dt$ where dy/dt is the strain rate, and the spring follows the equation for Hooke’s Law (Eqn. 8) at short times. Another material property is described by the viscoelastic-solid, which is more applicable for polymers at timescales $\tau_R \geq t \geq \tau_e$ and higher temperatures for the rubber plateau in Figure 7. To describe the viscoelastic solid, the Kelvin-Voigt model is used (see Fig 8b) where the Newtonian fluid and elastic properties are in parallel rather than in series. In this case, deformation by an external force is restricted by η and G , and relaxation is restricted by η but governed by G due to the force of the spring.

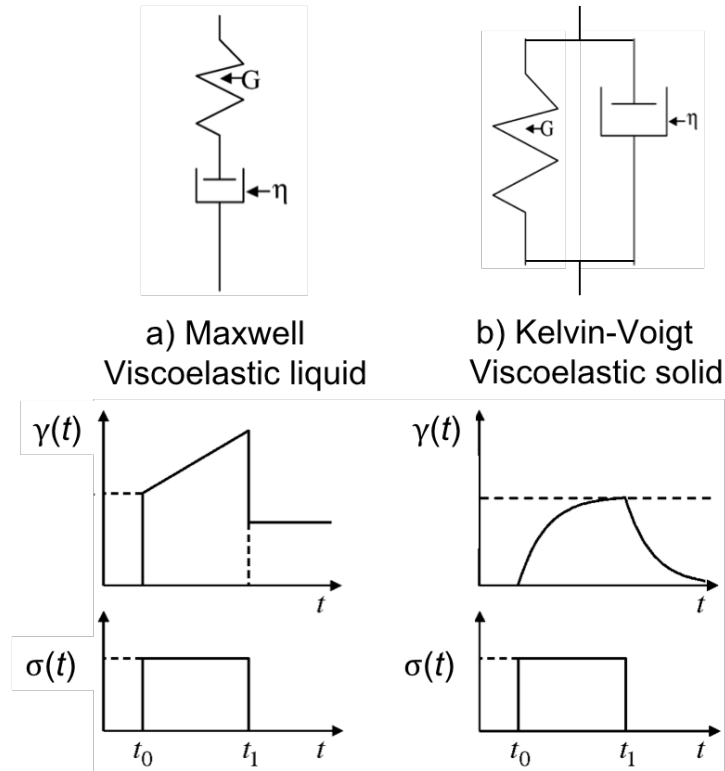


Figure 8: Simple models used to understand the viscoelastic liquid (a) and viscoelastic solid (b). Below each is the strain response γ to a time dependent stress σ to reveal the viscosity and elastic modulus through Eqns. 8 and 9. The stress and strain curves are adapted from [29] with permission.

The strain response to a stepwise stress is shown for the viscous liquid, elastic solid and the viscoelastic solid in Figure 8c. The responses to a sinusoidal stress will be covered briefly in Chapter 2. For now, the notable aspects of the polymeric viscoelastic solid are the material's ability to not only resist flow but to reform its original shape after deformation. This "memory" is an important characteristic of many polymer systems and occurs at the length-scales of cooperative chain dynamics and at timescales associated with topological entanglements of the relaxing chains. Since the motion of polymer chains is the main focus of this dissertation, the next sections will build off of the segmental motions of the dynamic glass transition that are described here but will focus primarily on the motion of chains.

There have been many studies that observe confinements at the lengthscales of ξ and the glass transition. However, this dissertation maintains a focus on confinements concerned with the dynamics at the lengthscale of the polymer chains to expand on the knowledge from studies that have also experimentally probed the dynamics of the polymer chains. While experiments that study the dynamic glass transition do look at the effects of polymer size, this effect is much more sensitive for the dynamics associated with the polymer chain. Therefore, it is important to consider the chain size and dispersity of sizes from Eqns. 1 and 2 for a polymer sample under investigation. As will become clear in the following sections, changes to the size of chains in a polymer sample can drastically alter the length-scales of entangled chains and the properties associated with elastic recovery. As such, the theory that describes these chain motions will now be summarized by the models of the Rouse chain and the entanglement Tube.

The Gaussian Chain: Normal Modes and Rouse Theory

As stated in the introduction, the Langevin equation which describes Brownian motion is the basis of the unrestricted dynamics. When additional forces are

included in this equation, or confinements on motion are included, the interesting properties that were covered in the previous section begin to emerge. In this section the theories that are used to describe the restricted Brownian motion of homopolymer chains will be defined along with the normal modes of the polymer chain using statistical methods. First the definition of the normal modes of a chain will be derived. Then, the Rouse model will be described, which uses the static conformation of the freely joined chain as demonstrated in the previous section and combines this with Gaussian statistics. Additionally, rather than rigid bond vectors, each Kuhn segment is connected by a spring which introduces forces to the random motions of each segment and connects this to the normal modes of a simple coupled harmonic oscillator system. However, the Rouse model is only accurate for real polymers up to a certain number of repeat units. To extend this theory for polymer chains of all sizes, more confinements that follow Gaussian statistics are included to ultimately give a fully incorporated picture of the Gaussian chain model and the normal modes of polymer chains.

To begin, the normal modes of a simple system of the motion of coupled harmonic oscillators will be derived when an external force displaces them and is removed, then the oscillators eventually return to equilibrium positions due to the nature of the springs that connect them. First a single bead of mass m on a spring with constant, k_s , has a one-dimensional time dependent position $q(t)$. The angular frequency of oscillation of the bead's position is defined by $\omega = (k_s m^{-1})^{1/2}$ to give the time dependent position by

$$q(t) = A \sin(\omega t + \phi) \quad 10$$

where A is the amplitude of displacement defined by initial conditions, and ϕ is the phase. With the force from the spring on the oscillator given by $F(q) = -k_s q = -dU(q)/dq$ (where $U(q)$ is the spring's potential energy), the second-order, homogeneous linear ordinary differential equation (ODE) of motion is given by

$$d^2q/dt^2 + \omega^2 q = 0 \quad 11$$

which has the solution below of an undamped harmonic oscillator for initial conditions $t=0$ and $dq(0)/dt = 0$

$$q(t) = q(0) (\cos \omega t + \omega^{-1} \sin \omega t) \quad 12$$

For additional, identical oscillators connected to the original oscillator by additional springs, the motions are coupled by a system of ODEs. Each oscillator may move at its own independent frequency. A specific set of solutions to this system of ODEs is defined for the oscillating masses with characteristic frequencies. For a system of i oscillators, there are i solutions to this eigenvalue problem. For simplicity, a system of two oscillators will be an example, as shown in Figure 9 with the central spring of constant k_s . This system of two ODEs is

$$d^2q_1/dt^2 + \omega^2 q_1 + (\omega')^2 (q_1 - q_2) = 0 \quad 13a$$

$$d^2q_2/dt^2 + \omega^2 q_2 + (\omega')^2 (q_2 - q_1) = 0 \quad 13b$$

The characteristic equation shown below has a characteristic frequency Ω for coupled motions

$$(\omega + (\omega')^2 - \Omega^2)^2 - (\omega')^2 = 0 \quad 14$$

which is satisfied by the eigenvalues $\Omega^2 = \omega^2$ and $\Omega^2 = \omega^2 + 2(\omega')^2$. In such a case, the two normal modes given below in Eqns. 15 are solutions to Eqn. 13 where Eqn. 15a states the motion of both oscillators have the same direction, amplitude ($A_1 = B_1$) and frequency ($\omega = \omega'$), and Eqn. 15b states the motion of the oscillators is in the opposite direction with $A_1 = B_1$ and $\omega = \omega'$ as shown in Figure 9b for $i = (-1)^{1/2}$.

$$\begin{pmatrix} q_1(t) \\ q_2(t) \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \end{pmatrix} A_1 e^{i\omega t} + B_1 e^{-i\omega t} \quad 15a$$

$$\begin{pmatrix} q_1(t) \\ q_2(t) \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \end{pmatrix} A_2 e^{it\sqrt{\omega^2 + 2\omega'^2}} + B_1 A_2 e^{-it\sqrt{\omega^2 + 2\omega'^2}} \quad 15b$$

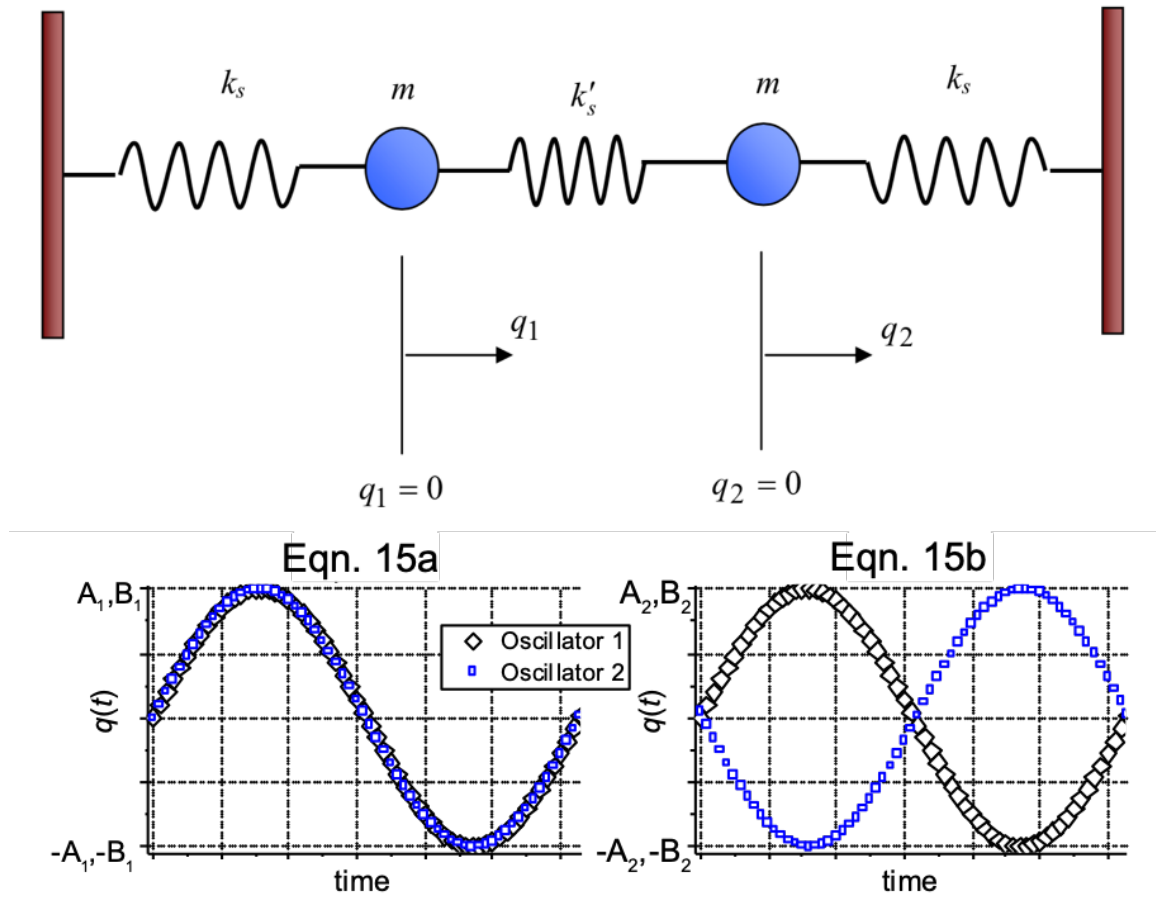


Figure 9: System of coupled harmonic oscillators at positions q_1 and q_2 with identical masses m and separated by Hookean springs with constants k_s or k'_s . The motions of these oscillators are solved over time where the specific solutions to this motion exist, called normal modes shown in the waveform plots, at coordinated frequencies. The top figure is reproduced from [30].

Now, with the basic foundation of normal modes of harmonic oscillators covered, the normal modes of a specific system of n coupled harmonic oscillators will be described as laid out by Rouse. For a Rouse chain, there are n oscillators in the chain separated by a vector with a length equal to the Kuhn segment length (this is essentially the freely joined chain). For clarification these oscillators are numbered with integer values j and are located at $\mathbf{r}_j$ which is connected to neighboring oscillators by two bond vectors $(\mathbf{r}_{j+1} - \mathbf{r}_j)$ and $(\mathbf{r}_j - \mathbf{r}_{j-1})$. The total chain end-to-end vector $\mathbf{R}$ will be a function of n as well as t . The primary difference between the random walk and the Rouse chain is the probability distribution function $P(\mathbf{R}(n,t),n)$ for the possible states of the chain conformation which follows Gaussian statistics in the central limit theorem over time as a function of the chain end-to-end vector and n [31].

$$P(\mathbf{R},n) = (3/2\pi nb^2)^{3/2} \exp(-3\mathbf{R}^2/2nb^2) \quad 16$$

The conformational entropy associated with this probability in relation to some reference entropy S_0 is found by incorporating all possible orientations as shown by

$$S(\mathbf{R}(n,t)) = k_b \ln P = S_0 - 3k_b \mathbf{R}^2/2nb^2 \quad 17$$

where the Boltzmann's constant $k_b = 1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$. An increase in $\mathbf{R}$ involves a decrease in entropy by Eqn. 17. The fluctuation dissipation theorem states that local friction of motion, which is governed here by entropy, causes heat to be dissipated to the surroundings [31]. From basic thermodynamics, a Legendre transformation can be taken of the internal energy with no interaction potentials in an incompressible system to give the temperature dependent free energy change associated with chain stretching

$$\Delta G(\mathbf{R}(n,t)) = 3k_b T \mathbf{R}^2/2nb^2 \quad 18$$

This change in free energy is derived from the chain acting as an entropic spring that exerts a force on its surroundings when it deviates from the ideal, random walk conformation. In other words, when the chain is stretched the possible conformations decrease, and the work done upon return to equilibrium is not due to a relative increase in internal energy, but from entropy. Therefore, this spring-like entropic force from the entire chain is derived in a similar way as was used to derive Eqn. 11 to give

$$\mathbf{F}_k = K \mathbf{R} \quad 19$$

where the harmonic spring constant $K = (3k_b T n^{-1} b^{-2})$. This result is different from the use of Hookean springs to connect the oscillators in that the forces increase as temperature increases due to the free energy change associated with entropic chain stretching. In addition to the entropic spring force that directs the oscillators' motions, there is the random stochastic forces $\mathbf{f}(t)$ that follows the classic Brownian motion by

$$\langle \mathbf{f}(t) \rangle = 0 \quad 20a$$

$$\langle \mathbf{f}_i(t) \cdot \mathbf{f}_j(t') \rangle = 2\zeta k_b T \delta_{ij} \delta(t - t') \quad 20b$$

where δ is the Kronecker delta such that there is no spatial or temporal correlation for Brownian motion, and ζ accounts for random friction among neighboring segments over time. This friction is also included in the force associated with motion that is imparted by the segmental relaxations at fast times as described in the previous section for the dynamic glass transition. This friction factor is $\zeta = 6\pi\eta a_h$ where a_h is the size of the oscillator between bond vectors. The limiting case for the Rouse chain is $a_h = b$, but this has been shown experimentally to not necessarily be true for real polymers.[32]

The Langevin equation for the coupled harmonic motion of j^{th} oscillator $\mathbf{r}_j(n,t)$, which we will now call a Rouse segment, can be written with the entropic

spring, friction and stochastic forces defined above (assuming inertial forces to be negligible)

$$\zeta \frac{\partial \mathbf{r}_j(n,t)}{\partial t} = K \frac{\partial^2 \mathbf{r}_j(n,t)}{\partial t^2} + \mathbf{f}(t) \quad 21$$

Since there is no use in solving Eqn. 21 in the continuous limit because each segment in the chain is finite, the solutions are found as a linear combination of n normal modes analogous to Eqns. 15 (in this case they are called Rouse modes) given by

$$\mathbf{X}_p(t) = N^{-1} \sum_{j=1}^n \mathbf{r}_j \cos[\pi p(j-1) n^{-1}] \quad (\text{for } p = 0, 1, \dots, n-1) \quad 22$$

The set of normal mode solutions are by definition orthogonal, and the normal mode associated with the chain's center of mass is for $p=0$ ($\cos 0 = 1$). The correlations among the normal modes $p \geq 1$ of segments in a single chain are given by an exponential decay and is called the Rouse chain autocorrelation function $C_R(t)$ below for sufficiently long chains ($n \gg p$)

$$C_R(t) = \langle \mathbf{X}_p(t) \cdot \mathbf{X}_p(0) \rangle = nb^2 [2\pi^2 p^2]^{-1} \exp(-t / \tau_p) \quad 23$$

The characteristic decay times for each mode are defined as $\tau_p = \tau_s n^2 p^{-2}$. Here $\tau_s = \zeta b^2 (3\pi^2 k_b T)^{-1}$ is the characteristic relaxation time of individual segments of the Rouse chain and is analogous to τ_α from the previous section (*cf* Eqn 9). The eigenvalues of the normal modes are $\omega_p = \tau_p^{-1}$ and will become important in connecting the dielectric response to the normal modes in Chapter 2. The $p=1$ normal mode is the reorientation of the end-to-end vector of the chain (*i.e.* terminal relaxation) and has a characteristic time τ_R termed the Rouse time (*cf* Fig. 7) and occurs at the longest times where the polymer system flows as modeled by the Rouse chain.

$$\tau_R = \zeta b^2 n^2 [3\pi^2 k_b T]^{-1} \quad 24$$

By neutron spin echo experiments, the high p Rouse modes occur for subchains at wavelengths $\sim n/p$ at lengthscales of $[nb^2/p]^{1/2}$ [27].

Now the specific location of each Rouse segment can be calculated by taking the inverse transform of Eqn. 22 to find

$$\mathbf{r}_j(t) = \mathbf{X}_0(t) + 2 \sum_{p=1}^{n-1} \mathbf{X}_p \cos(\pi p(j-1/2) n^{-1}) \quad 25$$

where $\mathbf{X}_0(t)$ is the normal mode for the chain's center of mass. Using these equations, the total end-to-end vector of the chain as a function of the number of segments and over time can be calculated and rearranged to give

$$\mathbf{R}(n,t) = \mathbf{r}_n - \mathbf{r}_0 = -4 \sum_{p:odd}^{n-1} \mathbf{X}_p(t) \cos(\pi p/2n) \quad 26$$

Thus the autocorrelation function of the $\mathbf{R}(n,t)$ over time is (discounting even modes which average out to zero due to motional symmetry)

$$\langle \mathbf{R}(n,t) \cdot \mathbf{R}(n,0) \rangle = 2b^2 n^{-1} \sum_{p:odd}^{n-1} \cot^2(\pi p/2n) \exp(-t/\tau_p) \quad 27$$

Again, for the assumption that $n \gg p$, the cotangent term above reduces to p^{-2} which indicates that the slowest normal modes of the Rouse chain are the dominating contributors to Eqn. 27. The slowest mode, here $p = 1$, is then used as the global end-to-end dynamics of the chain.

For some microscopic deformation, σ has been approximated in terms of the Rouse modes in a planar shear (xy) with some number of chains N within a volume V by [4]

$$\sigma_{xy}(t) = [3Vk_bT / Nb^2] \sum_{p=1}^N \langle \mathbf{X}_{p,x}(t) \mathbf{X}_{p,y}(t) \rangle 2\pi^2 p^2 N^{-1} \quad 28$$

By combining this with Eqn. 8 but for an oscillating mechanical force in the linear regime, the frequency-dependent, complex shear modulus, $G^*(\omega) = G' + iG''$, may be obtained using a Fourier transform to combine the physical properties of polymeric systems with respect to the theoretical dynamics of the Rouse chain.

$$G' = \sum_{p=1}^{n-1} \frac{\omega^2 \tau_p^2 / 4}{1 + \left(\omega^2 \tau_p^2 / 4 \right)} \quad 29a$$

$$G'' = \sum_{p=1}^{n-1} \frac{\omega \tau_p / 2}{1 + \left(\omega^2 \tau_p^2 / 4 \right)} \quad 29b$$

For real polymer systems, the Rouse model breaks down after the chains contain more than N_e segments. That is because using the Langevin equation (Eqn. 21) produces the Einstein equation for diffusion for the Rouse chain at long times. Thus, there is no consideration for terminal relaxations of chains that begin to topologically interact or entangle. Without this consideration, the rubber plateau in Figure 7 cannot be modeled for the Gaussian chain.

As mentioned above, the Rouse chain only overcomes the freely joined chain by a Gaussian distribution for its available chain conformations. While it does consider frictional forces due to the dynamic glass transition, it does not include physical or chemical interactions of the chains. Considerations for physical chain entanglements were proposed by de Gennes who was awarded the 1991 Nobel Prize in physics for the Reptation model. This model incorporates constraints to chain motion due to the overlap of neighboring molecules at nodes along the chain contour. This was later incorporated into the Rouse theory by Doi and Edwards who included contour length fluctuations which gives a lifetime to the nodes to account for enhanced mobility of the neighboring chains' chain-ends compared to entanglements among central subchains [4, 13, 16, 33]. The combination of these considerations is articulated through the Tube model and has been expanded upon to also include postulates for dynamic tube dilation and constraint release to include theoretical predictions of homopolymer dynamics for branched systems and materials with a high dispersity by Eqn. 2 [34-38].

For the linear chain in the Tube model, the nodes of constraint mentioned above are modeled as a tube with diameter $d \sim b\sqrt{N_e}$ in which a Rouse chain that

contains N_e segments resides [39]. The time dependence of the mean square displacement of a segment $\langle r_j^2 \rangle$ in a monodisperse system is shown in Figure 10 at different regimes that account for effects of the confined motion of a segment by a tube that is modeled to describe the surrounding matrix of chains and their constraints on the test segment. This tube follows the primitive path of the chain with a contour length of L which is shown as a dotted red line in Figure 10. At fast times, the segments have Brownian (Rouse-like) diffusion with characteristic timescales of τ_s and are unconstrained by the length-scales of d (or a root mean square segment displacement $\langle r_j^2 \rangle = d^2$ as shown in Fig. 10). At a characteristic entanglement timescale $\tau_e \propto \tau_s N_e^2$, the segments are given enough time so that they have at least diffused to the lengthscale of d and have interreacted or are constrained in space by the tube (see Eqn. 30a). Next, is the reptation timescale for the segments τ_R (which scales similarly to entanglement by number of chain segments) where the dynamics of segments are still confined by other chains or within tube but the global movement of segments along the primitive chain contour occurs. For reptation, each Rouse segment stays inside the tube, but the primitive chain relaxes by changing its average position at a rate of $\omega_R = \tau_R^{-1}$ giving rise to the importance of the timescale of the tube's motion. Lastly, the disentanglement timescale τ_d ($\propto \tau_s N^3$, and see Eqn. 30b) is such that the average position of the tube or primitive chain is uncorrelated with its previous position and is termed the terminal relaxation of the chain and is the $p=1$ normal mode for the Tube model. The more general characteristic relaxation time as a function of normal mode p is given in 1.30c.

$$\tau_e = \zeta d^4 (k_b T b^2)^{-1} \quad 30a$$

$$\tau_d = \zeta b^4 n^3 / \pi^2 k_b T d^2 \quad 30b$$

$$\tau_p = \zeta b^4 n^3 / \pi^2 k_b T d^2 p^2 \quad 30c$$

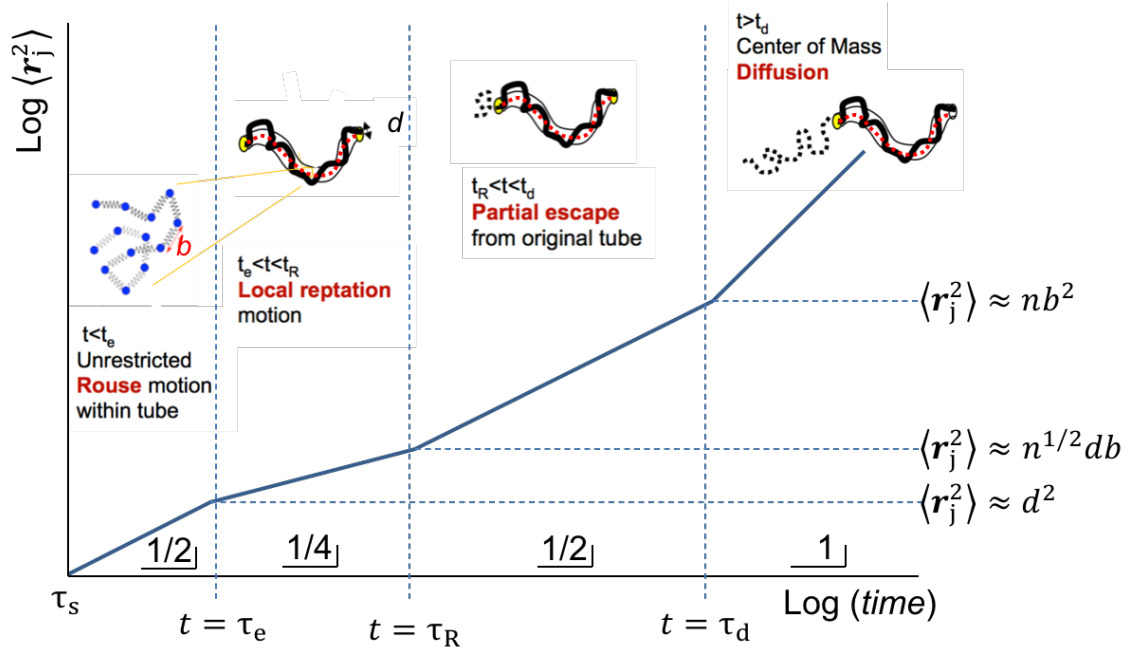


Figure 10: The time dependence of the Gaussian chain segment position shown in different regimes as modeled by the Tube model of the Rouse chain (a) and schematics depicting the lengthscales of the segments and chain in the tube. The cartoons for each regime are adapted from [40].

The number of entanglements of a Rouse chain is given by $Z = \tau_d \tau_R^{-1} = 3b^2nd^{-2}$. The for a polymer of molecular weight M , the molecular weight between entanglements for a real polymer M_e for $M_e = MZ^{-1}$ as modeled by the Rouse chain and the characteristic ratio follows [39]

$$M_e = 864n^2M_0^3 [C_\infty(lb\rho)^2]^{-1} \quad 31$$

where n is the molar amount of repeat units in the chain, M_0 is the repeat unit molecular weight, $\rho = N/V$ is the number density of chains, C_∞ , l and b are from Eqn. 6, and N_{av} is Avogadro's number. The molecular weight at which the entangled chains begin to disentangle at τ_d for the terminal relaxation is $M_c \sim 2M_e$. The viscosity for flow behavior of polymer chains, calculated for the Rouse chain and Tube model by $\eta_0 = G_N \tau_d$, where $G_N = \lim_{\omega \rightarrow \infty} G''\omega^{-1}$ is the modulus value of the rubber plateau as calculated G'' from Eqn. 29b, is plotted against molecular weight for the theory and for several real polymers in Figures 11a and 11b, respectively. The experimental findings shown still deviate from the entangled Rouse chain and segment reptation. The contributions of dynamic tube dilation (DTD) and constraint release (CR) have been used to model this deviation, and the mechanisms of these are displayed in Figure 11. The DTD allows for some internal segments to have longer τ_e by increasing d for subchain segments due to CLF and reptation of other chains which imparts a distribution to this timescale. The CR mechanism allows for the tube to be discontinuous along the chain contour for some time allowing for subchains between entanglement nodes to relax, but then the tube reforms to be continuous again. These aspects are also considered and briefly introduced in Part I to describe the dynamics of block copolymer systems.

Finally, the conformational entropy of the primitive chain, and thus the Rouse chain under topological entanglement and contour length fluctuation confinements at $t < \tau_r$, is based on the parameters of the tube and the chain flexibility by Eqn. 32 below [4]

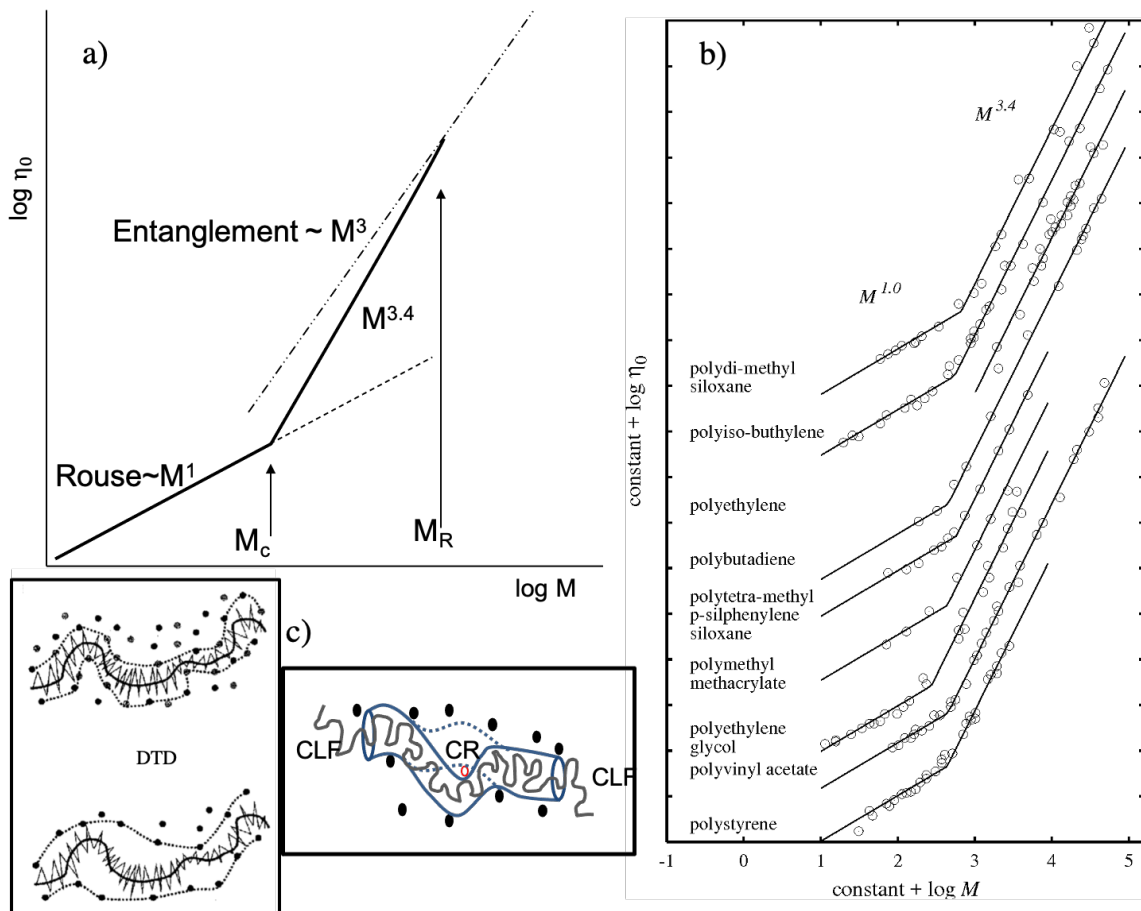


Figure 11: The chain molecular weight dependence of zero shear viscosity predicted for entangled Rouse chains (dashed lines) in comparison with experiment (solid lines). At M_R entanglement dynamics have altered into fully reptation (a). Examples of η_0 data measured for real polymer systems (b, adapted with permission from [41]). The schemes in (c) at the bottom left, depict mechanisms of contour length fluctuations (CLF) at the chain ends, constraint release (CR) for the midchain where the red constraint no longer exists allowing the tube to rearrange, and dynamic tube dilation (DTD) where the diameter of the tube is dependent on the space between the constraints along the chain contour. The DTD cartoon is used with permission from [42].

$$S_c(L) = S_0 - k_b [(3L^2/2nb^2) + (\pi^2 nb^2/3d^2)] \quad 32$$

This entropy is decreased compared to the Gaussian entropy (*cf* Eqn. 17) which was purely based on the conformational states of the freely joined chain. This decreased entropy for the entangled chain segments increases the entropic force on the surroundings and predicts that a material that consists of entangled polymer chains have a greater mechanical strength than a material with chains that follow the Rouse model.

Dielectrics and Chain Dynamics

An interesting analogy of a chain's normal modes by Rouse is found in the quantum mechanical equation by Schrödinger in that it solves for a time dependent wave function that describes position, and there are discrete eigenfunctions f_i that become dominated by the ground state, or zeroth mode f_0 , just as the Rouse mode dominates the correlation function in Eqn. 23. Using this quantum mechanical analogy, the entropic free energy of a system with volume V and large number of segments n is given by

$$S_e/k_b T = b^2 n (6V)^{-1} \int |\nabla f_0(\mathbf{r})|^2 d\mathbf{r} \quad 33$$

where ∇ is the three-dimensional gradient scalar to map the space of the eigenfunctions. One of the primary experimental techniques that has been used to determine the eigenfunctions and normal modes of polymer chains is dielectric spectroscopy, which is detailed in Chapter 2. For now, the segmental and chain relaxations of real polymer chains will be explored from various experimental and mathematical studies along with predictions and relationships to the normal modes of polymer chains and material properties. This section will provide a summary of

some major findings for dynamics of homopolymer systems using dielectric spectroscopy and other methods.

First, the types of relaxation must be clarified in the context of types of experimental measurement techniques and mathematical models that describe them. The material response from mechanical perturbation is similar to that by electric field, however, a material's response to mechanical deformation is related to the isochronal orientational anisotropy of segments by an orientation function whereas the dielectric response relates to orientational correlations of segments over time by the local correlation function [43, 44]. Either way, the motions of polymer molecules within material are probed by some externally controlled, time-dependent force. When that force is removed, the rearrangement of the molecules back to equilibrium is termed relaxation. Different molecular motions are associated with different lengthscales with polymer side-groups, segments and chains all being probed at different timescales. When the temperature is increased or decreased, specific fluctuations become faster or slower, respectively. Also, portions of a molecule at intermediate lengthscales, like sub-chain relaxation, may become faster or slower, or may contribute more or less to the response measured experimentally due to topological restrictions to random motion. Within the fluctuation dissipation theorem, the cooperative reorientation of segments in response to a relatively small displacement gives rise to relaxations that are analogous to random equilibrium fluctuations. These relaxation responses measured for random fluctuations are in contrast with quasi-elastic scattering measurements which directly measure these fluctuations without applying a field, but have been shown to represent the same dynamics[45].

For polymer dielectric relaxations, the orientation of monomeric dipoles with respect to the polymer backbone is an important consideration when identifying the relaxations measured dielectric spectroscopy at different timescales. Polymeric dipoles are recognized by the chemical structure of the monomeric units and side groups. The various types of monomeric dipoles μ have been defined by

Stockmayer with respect to their orientation to the polymer backbone and are shown in Figure 12. The type-A polymer chain contains dipoles that are within and oriented parallel to the polymer backbone $\mu^{\parallel}$. The type-B polymer chain contains dipoles that are within the polymer chain, but are oriented perpendicular to the backbone $\mu^{\perp}$. This relaxation is typically associated with the segmental relaxation (eg. structural relaxation or α relaxation) at the timescale of τ_{α} which for polymers is equivalent to τ_s in Eqn. 23. Finally, there is type-C where dipoles may be oriented in any direction with respect to the polymer backbone and is not a part of the polymer chain but is within the side group μ^C . The type-C polymer dipole does not insinuate that the dipolar motion is uncorrelated with the relaxation of the chain, but this dipole type does not give direct observation to relaxations of the main chain at any particular lengthscale.

Type-A polymer chains, which for all intents and purposes always have a portion of the monomeric dipole moment that is also perpendicular to the main chain (ie Type-AB), allow for the polymer chain relaxation and segmental relaxations to be probed experimentally by dielectric experiments. Simulations and experiments show that for the relaxations of segments and the chain end-to-end to have no cross-correlation, the real chain must be analogous to a Rouse chain with more than 10 total segments [46, 47]. When the parallel orientation of the monomeric dipoles with respect to the main chain are all in the same direction, these dipoles may sum to form a chain end-to-end dipole. If the direction of parallel dipole orientations is inverted along the contour of the chain, the response will correspond to subchain relaxation and relate to normal modes that are not the $p=1$ total chain end-to-end mode. Therefore, the summed relaxations of $\mu_{\parallel}$ are associated with the timescales modeled for the normal modes by Rouse and de Gennes in the sections above.

Much of the experimental work of the dielectric chain relaxation within the context of the theoretical work was performed by Adachi, Kotaka, Watanabe and coworkers and is summarized below.

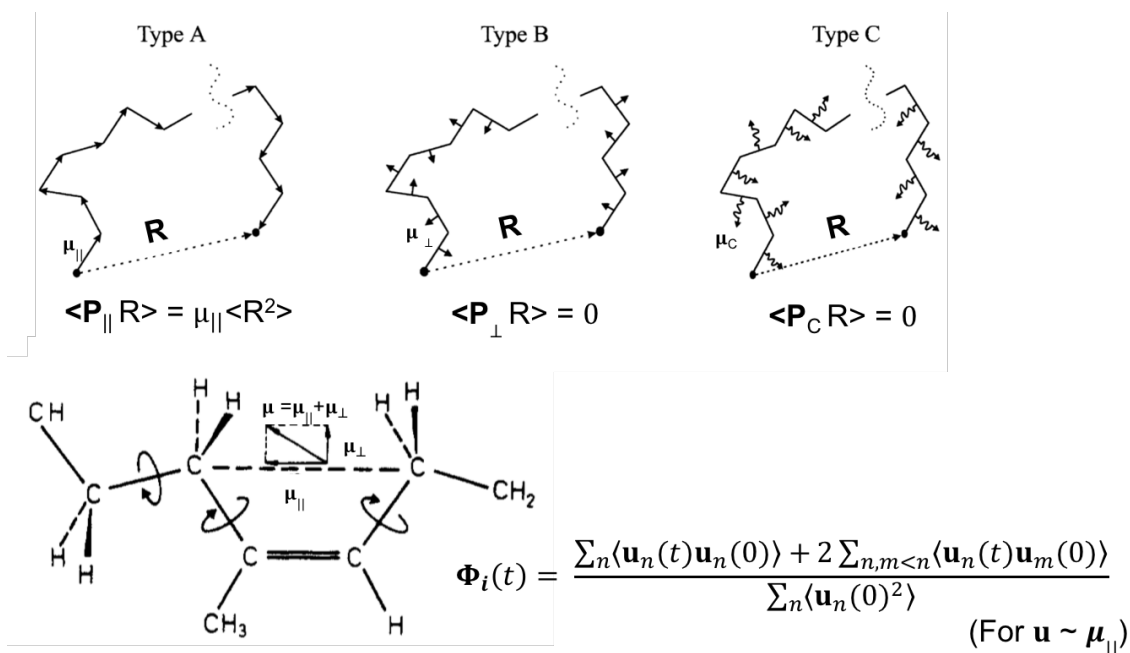


Figure 12: Characteristic dipole orientations for Type-A, -B, and -C polymers and their relationship with the size of the end-to-end vector polarization (top). Also shown is the monomeric dipole moment of poly(*cis*-1,4-isoprene) separated into parallel and perpendicular portions, along with the response function of chain i with orientational correlations among monomeric/segmental bond vectors u_n including cross-correlations from Eqns. 34 and 36. PI monomeric dipole moment diagram is used from [48] and polymeric dipole images are adapted [49], both with permission.

The studies described here, as well as the case studies of the chain dynamics in this dissertation, utilize the prototypical Type-AB polymer, poly(*cis*-1,4-isoprene) (from here will be abbreviated as “PI”) whose monomeric dipole is shown in Figure 12 [48].

To model the Type-A chain from Figure 12, the local correlation function for the motions of n^{th} and m^{th} segmental bond vectors in the i^{th} polymer chain ($\mathbf{u}_i(t)$) are mathematically described using the local correlation function $C_i(n,t)$, which was defined as the autocorrelation function for the Rouse chain C_R in Eqn 23 without cross-correlations between segments in neighboring chains. Often, these cross-terms are negated, but they will be considered here for generality giving the local orientational correlation function over all chains

$$C_i(n,t) = \sum_i \left\langle \frac{\sum_n \langle \mathbf{u}_i(n,t) \cdot \mathbf{u}_i(n,0) \rangle + 2 \sum_{n,m < n} \langle \mathbf{u}_i(n,t) \cdot \mathbf{u}_i(m,0) \rangle}{u^2} \right\rangle \quad 34$$

where $u = \sqrt{\langle \mathbf{u}(t)^2 \rangle}$ is the average length of segmental bond vectors (analogous to the Kuhn segments in the previous section). Based on the precedence set by Watanabe and coworkers, we use Eqns. 35a and 35b to define the boundary conditions of this local correlation function at the chain ends (0 and N) and for very fast times ($\tau \rightarrow 0$), respectively, and in Eqn. 35a for C_i in terms of the eigenfunctions of the normal modes f_p [50-54].

$$C_i(n, t; m) = 2N^{-1} \sum_{p=1}^N f_p(n) f_p(m) e^{-t/\tau_p} \dots = 0 \text{ for } n=0 \text{ and } m=N \quad 35a$$

$$C_i(n, 0; m) = \delta_{nm} \quad (\text{Kronecker delta}) \quad 35b$$

In Eqns. 35a and 35b, f_p is the p^{th} eigenfunction with τ_p as the characteristic relaxation time. When evaluated at long times, the eigenfunctions of $C_i(n,t)$ describe the response function $\Phi(t)$ of the entire chain (see Eqn. 36 below and the equation in Fig. 12), which can then be decomposed into distinct normal modes of the chain and used to gather information about the global motion of the Type-A

polymer[54-56]. For more information regarding the how Eqn. 36 relates to complex dielectric function ϵ^* , see Ch 2.

$$\Phi(t) = N^{-1} \iint_0^N C_i(n, t; m) dn dm \quad 36$$

In the late 1980's and early 1990's, PI was studied using several experimental methods to correlate real polymer responses with the Rouse and Tube theories. Figure 13A shows the dielectric relaxation spectra of PI over a wide frequency range for many molecular weights. At higher frequencies a relaxation that corresponds with the segmental motion is observed to be independent of polymer size. Because the average chain end-to-end fluctuation is dependent on the number of segments in the chain, and its characteristic time corresponds to the $p=1$ mode, the slower chain relaxation was reported to roughly follow the dynamics of the Rouse chain which gets slower with increasing chain size. In Figure 13B the shape of the dielectric chain relaxation of PI is shown to change slightly with molecular weight (Fig. 13B1), but is very dependent on PDI of the sample under investigation (Fig. 13B2) [57-61]. This is because the dielectric relaxation of the PI chain is an average of all chains in the material. In the late 1990's a series of studies were published by Watanabe and coworkers that focused on determining the eigenfunctions of poly(cis-1,4-isoprene) homopolymer, and to alter the normal modes contributing to experimental dielectric relaxations[50, 52, 56, 62-64]. In these works, the orientation of μ in the PI backbone was inverted at some location n^* in the polymer backbone, where a symmetric inversion of the chain end to end dipole would occur for at $N/2$.

These studies showed that the PI chain relaxation measured by dielectric spectroscopy could be modified based on the dipole moment orientation to reflect the normal modes of the chain. With altered direction of the dipoles, the normal modes relating to the relaxation function in Eqn. 36 can be described by Eqn. 37 below.

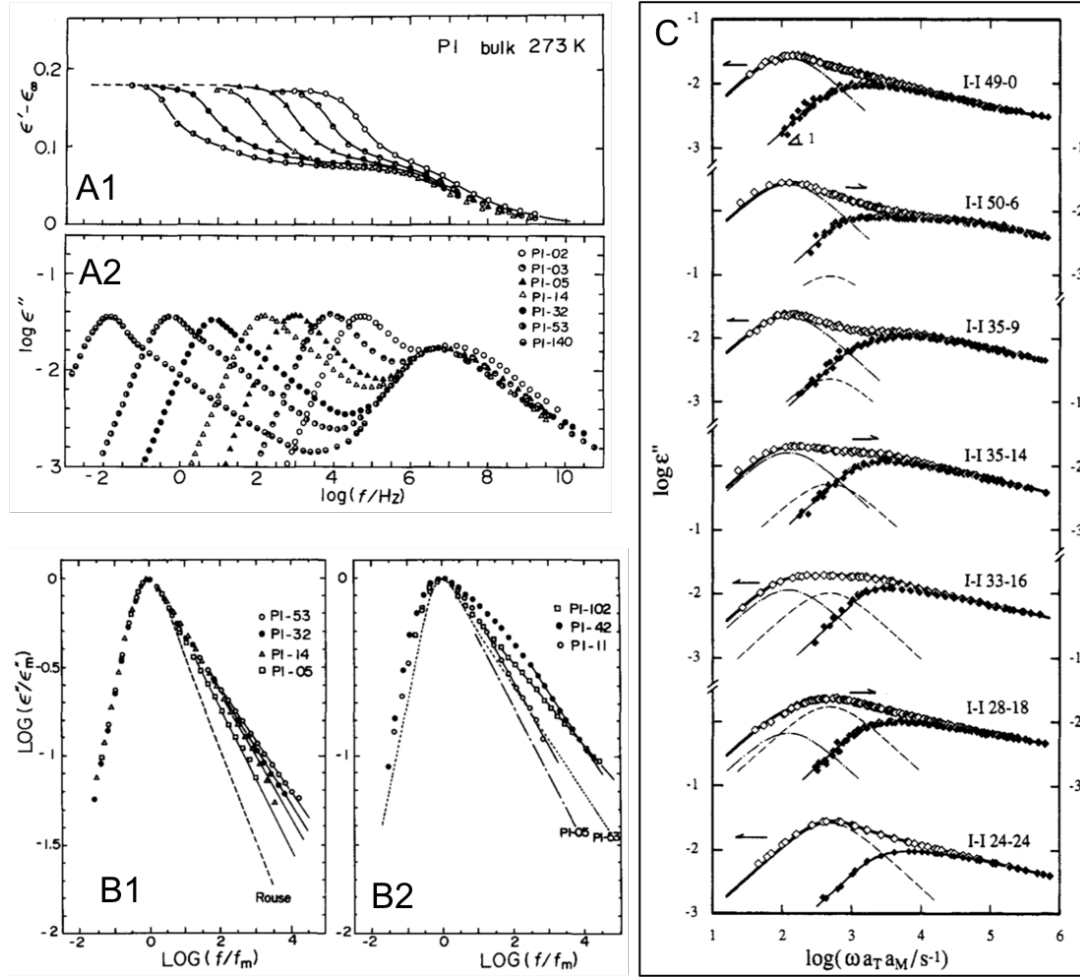


Figure 13: Panels A1 and A2 show the real and imaginary parts of the complex dielectric function for bulk linear PI with different molecular weights at 0°C. The high frequency peak is the segmental relaxation and essentially molecular weight independent; the slower chain relaxation moves toward lower frequencies as the polymer size increases. The corresponding peak times $\tau_{\text{peak}} = (f_{\text{peak}})^{-1}$ may be represented in right panel of Fig. 11. Panel B1 compares the shapes of the chain relaxation for monodisperse PI samples as molecular weight changes, and panel B2 shows chain relaxations of PI for PDIs of 1.08 (PI-102), 1.34 (PI-42) and 1.17 (PI-11). Panel C shows the imaginary part of the dielectric function for a 50kg/mol PI chain with varied inversion points for $\mu_{\parallel}$ with long dashed lines represent the $p=1$ mode and dashed lines represent $p=2$ and closed circle symbols for $p \geq 3$. Panels A and B are reproduced from [65] and C are reproduced from [50], both with permissions.

$$\Phi(t;n^*) = N^{-1} [\int_0^{n^*} dn - \int_{n^*}^N dn][\int_0^{n^*} dm - \int_{n^*}^N dm]C(n, t; m) \quad 37$$

As n^* approaches $N/2$, the dielectric response of the chain relaxation changes in shape and in frequency of the ϵ'' peak maxima, as shown in Figure 13C.

For dipole bifurcation at $n^* = N/2$, the dielectric chain relaxation reveals the even modes with the $p=2$ mode dominating the response and has $\tau_2 = 4\tau_1$ as modeled by Eqn. 30c. The integral $F_p = \sqrt{2} (N)^{-1} \int f_p(n)dn$ correlating the modes determined experimentally using Eqn. 35a, and also experimentally changing direction of monomeric dipole orientation at n^* showed that the mathematical description of the PI normal modes follow[64, 66]

$$\Delta F_p (n^*) = F_p (n^*) - F_p(N/2) = \sqrt{2} (\pi p)^{-1} [1 - \cos(\pi p n^*/N)] \quad 38$$

Equations 39a and 39b connect this summarily to the dielectric function with a factor g_p for the intensity of mode p as it contributes to the dielectric loss spectrum $\epsilon''(\omega; n^*)$ for relaxation contributions in an exponential form by

$$\epsilon''(\omega; n^*) = \sum_{p=1}^N g_p(n^*) \frac{\omega \tau_p}{1 + \omega^2 \tau_p^2} \quad 39a$$

$$g_p(n^*) = 2\Delta\epsilon N^{-2} [\int_0^{n^*} f_p dn - \int_{n^*}^N f_p dn]^2 \quad 39b$$

where $\Delta\epsilon$ is the dielectric strength of the relaxation measured by dielectric spectroscopy. All of this is to say that experimentally the normal modes of a Type-A chain may be determined for a system of monodisperse homopolymer chains. While the equations above are useful within this context, many more considerations must be made when the polymer chains are joined together into blocks and phase separated by thermodynamics of mixing. These effects to the dielectric response function in accordance with the normal modes described here are the primary focus of Part I of this dissertation.

These studies were of great importance in recognizing the effects of constraints on the chain dynamics of homopolymer systems and in connecting the theory to experimental perturbations. These effects have been expanded upon for entangled chains which show increased high frequency contributions to the chain relaxation due to higher order normal modes (subchain modes) constraining the motion of the chains as shown in Figure 13B1. This change in the dielectric chain relaxation shape is often the primary focus for recognizing confinement effects on the chain dynamics and normal modes. Numerous efforts have been made to model this entanglement constraint with the number of nodes Z that represents the topological of entanglements from Eqn. 31 [37, 38, 46, 67, 68]. The use of blending dilute polyisoprenes into a dielectrically inactive but thermodynamically similar polybutadiene matrix, which lacks the methyl group that affords measuring the Type-A PI chain, has shown how a single chain under various conditions can be measured to reveal the effects of the confining matrix [35, 42, 44, 64, 69-71]. Furthermore, the chain relaxations and normal modes of star homopolymers have been explored thoroughly to determine how branching constrains the dynamics of the chains. Ultimately, the characteristic relaxation time for the experimental chain relaxation represented by the frequency of the local maximum in the dielectric spectrum τ_n is shown to follow a $\sim N^3$ relationship as per Eqns. 30a-c, but then changes to $\sim N^{3.4}$ when the molecular weight is equal to the critical molecular weight M_c (see Figure 11).

The final experimental consideration that is discussed here and that has been the subject of many studies is the dynamic heterogeneity of the dielectric chain relaxation with respect to the relaxation times of the segmental relaxation. From the Rouse model, the normal mode relaxation time τ_p in Eqns. 23 and 30c has a temperature dependence based on the friction coefficient ζ of the segment which is used in the expression for τ_α . However, the experimental chain relaxation time τ_n is observed to have a weaker temperature dependence than τ_α (as shown in Chapter 4) resulting in heterogeneity in the dynamics at various lengthscales. This

problem has been approached by Shönhals and others by extrapolating the τ_n to low temperatures such that it becomes equivalent to τ_α and therefore the volumetric lengthscale of the segmental relaxation is equal to the root mean square end-to-end lengthscale of the chain ($\xi^3 = \langle \mathbf{R}^2 \rangle^{1/2}$)[72, 73]. Additionally, pressure dependent studies on PI dielectric relaxations have shown that the relative activation volume for the chain relaxation is smaller than that of the activation volume of the segment, and the shape of the chain relaxation is T independent with a slight P dependence for a given molecular weight[74-78]. This reveals that for the model describing these dynamics, the effective segment size b decreases with increasing pressure and thus the total number of segments N increases becoming more entangled for a smaller chain length [77]. This, however, does not mean the $\langle \mathbf{R}^2 \rangle$ changes and thus the experimental relationship of τ_n and N does not change. This dynamic heterogeneity is also discussed in terms of fragility, or the change in the slope of the relaxation time as the temperature approaches T_g . As mentioned, the τ_n and τ_α have different T-dependencies and therefore approach T_g at different rates.

Ultimately, the τ_n is shown to be dependent on topological interactions and C_∞ , and τ_α is dependent on the chemical structure and ζ , whereas the fragilities of τ_α and τ_n are controlled by the lengthscale of cooperative segmental motion ξ and the lengthscale of the entire molecule relaxation modeled by viscoelasticity measured by η [77-79]. Furthermore, for entangled chains at relatively short deformation times that measure equilibrium fluctuations, the chain is not observed to be able to access every available conformational state[78, 80, 81]. This case is extended for phase separated block copolymer systems, and is discussed in the Introduction to Part I. While most of this chapter is concerned with relating entropic effects to the dynamics of linear homopolymers, when homopolymers of different types are blended and/or chemically bonded together (*ie* block copolymers) enthalpy becomes important to consider as the mixture of two unlike systems tend to phase separate. The balance between entropic chain stretching and enthalpy of

mixing, and the resulting dynamical constraints that arise from this phase separation are detailed in the introductory sections of Part I as a continuation of the model dynamics and experimental findings that were presented in this chapter.

Chapter 2: Experimental Methods

When light, or electromagnetic radiation (EMR) at different frequencies shown in Figure 14, interacts with or is emitted from matter, the extraordinary properties of the physical world that are invisible to us are revealed. The basic fundamental theories of classical physics allow electrical and/or vibrational modes of atoms and/or molecules to be measured by observation of the change in energy associated with these vibrations at certain frequencies (f) that are dependent upon the wavelength (λ) of the illumination. These techniques are broadly called spectroscopy.

Initially, spectroscopic methods were limited to waves of the EMR spectrum in the frequencies of visible light. The wavelengths of EMR are associated with amounts of energy by $E=hc/\lambda$ where h is Planck's constant and c is the speed of light. Particular quantized energies may induce vibrations in matter based on specific characteristics. The perturbation to different parts of a molecule from an applied EMR is simply a result of a force F by $-\delta E/\delta x = F$. This applied spectroscopic force is time dependent by $F(t) = F_0 + A \sin(2\pi ft + \psi)$ where t is time and ψ is the initial phase of the applied force. This is analogous to Eqn. 19 in Chapter 1 for a system of harmonic oscillators of a Rouse chain, which connects polymer dynamics to spectroscopic methods.

As can be gathered, spectroscopy is not just limited to optical excitation but has been expanded to include other time dependent forces produced by all sorts waves not just within EMR. These include acoustic waves, waves produced purely by magnetic or electric fields or even mechanical waves. That is to say, ultimately, the measured response of a material to a force that is produced from a time dependent energy source is spectroscopy. This chapter primarily focuses on the method of broadband dielectric spectroscopy which applies an electric field force over the radio wave frequencies to measure the dynamics of free or bound charges within a molecular system and is used to measure the polarization relaxations in polymers for Part I and II of this dissertation.

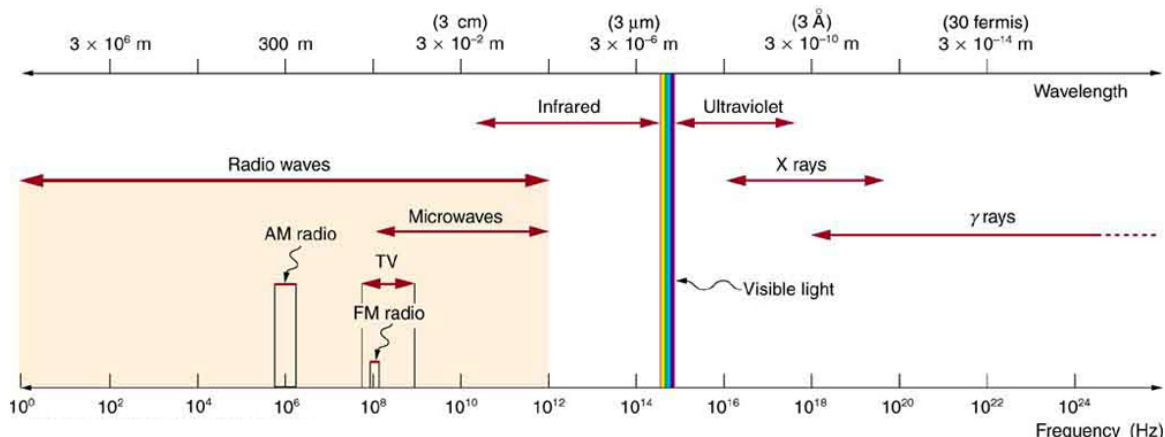


Figure 14: Shown here, the electromagnetic spectrum at various wavelengths, λ (top) and frequencies f (bottom) where $\lambda f = v$ where v is the phase speed, is the basis of spectroscopic methods. However, other time dependent forces can be applied to materials to probe their molecular structures and dynamics at different frequencies associated with these wavelengths. Image is reproduced from [82].

Other techniques of small angle x-ray scattering, transmission electron microscopy and Raman spectroscopy which are relied upon for substantial experimental results are also discussed in detail. Complementary techniques of differential scanning calorimetry and dynamic mechanical spectroscopy (which is introduced in some detail in Chapter 1 for Eqns. 8 and 28) are used in some instances in this dissertation but are not relied upon for specific conclusions and are strictly complementary to the results from the experiments that rely on the techniques described below.

Broadband Dielectric Spectroscopy

As mentioned briefly above, broadband dielectric spectroscopy (BDS) applies an electric field to a material and measures the response of dipoles within the material from the force associated with that field. The span of frequencies possible for BDS methods is remarkable ($10^{-6} - 10^{12}$ Hz) among other non-optical spectroscopies and is based on the polarizability of materials by an electric field. This section covers the theory that governs thermal dielectric processes in this frequency range, the types of motions associated with those dielectric processes and some of the fundamental experiments that have been published for dielectric and ion containing polymeric systems.

The theory of dielectrics stems from the Maxwell equations in Eqns. 40a-d where **B**, **E**, **D** and **H** are the induced magnetic field, the external electric field, the induced displacement electric field, and the external magnetic field.

$$\nabla \cdot \mathbf{B} = 0 \quad 40a$$

$$\nabla \times \mathbf{E} = -\partial \mathbf{B} / \partial t \quad 40b$$

$$\nabla \cdot \mathbf{D} = \rho_e \quad 40c$$

$$\nabla \times \mathbf{H} = \mathbf{j} + \partial \mathbf{D} / \partial t \quad 40d$$

The **H** and **B** and the current density **j** are not unconnected to the theory of dielectric, but rather are the mirrored quantities in the fundamental concepts used

in nuclear magnetic relaxation (NMR) spectroscopy and will be incorporated into the discussion later with respect to ion motion. For BDS, the primary fundamental concept is the induced dielectric displacement vector field $\mathbf{D}$ in Eqn. 40c. The divergence of $\mathbf{D}$ in Eqn. 40c is equal to the charge density $\rho_e = (dQ/dV$ where Q is sum of all charges $q, Q = \sum q$ within a volume V) and is otherwise known as Gauss's law. Gauss's law describes the dispersion of free charges within a volume that results from the applied electric field $\mathbf{E}$. This is derived from the electric field flux Φ_E , or rather the magnitude and direction of the forces $\mathbf{F}$ applied by $\mathbf{E} = \mathbf{F}/q$, through a surface as visualized in Figure 15.

Rather than taking the integral form in the equation from Figure 15 over a surface, the differential form over a specified volume results in an equivalent form of Eqn. 40c by

$$\nabla \cdot \mathbf{E} = \rho/\epsilon_0 \quad 41$$

where ϵ_0 is the permittivity of a vacuum ($\sim 8.854 \times 10^{-12} \text{ F m}^{-1}$). When the charges within a volume are not able to move freely but are bound, the material is susceptible to polarization, or simply an induced imbalance of charge within a volume due to the force on these charges from $\mathbf{E}$. So far, these quantities have been constant with time. For a frequency dependent, uniform field $\mathbf{E}(\omega) = E_0 e^{-i\omega t}$, where there is a sufficiently low potential difference of magnitude E_0 , $i = \sqrt{-1}$ and $\omega = 2\pi f$ is the frequency of the applied field in radians s^{-1} , the susceptibility to polarization is quantified by a linear relationship with the induced polarization over the entire material $\mathbf{P}(\omega)$ through the complex constant of proportionality $\chi^*(\omega)$, or the electric susceptibility and is related by

$$\mathbf{P}(\omega) = \chi^* \epsilon_0 \mathbf{E}(\omega) \quad 42$$

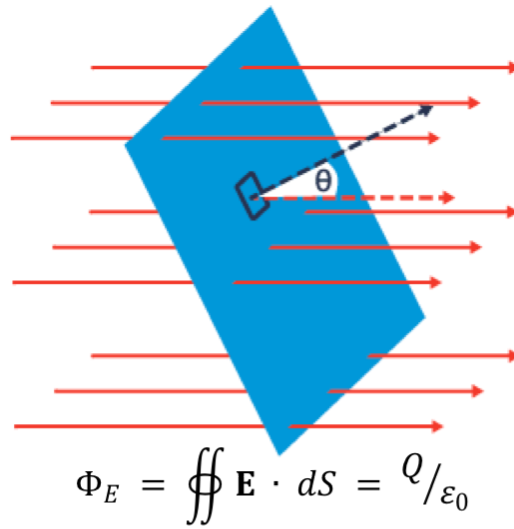


Figure 15: Schematic of Gauss's Law (adapted from [83] with permission). The electric field flux, depicted as force vectors by the red arrows, across a surface. When this surface is wrapped around to enclose some volume, the surface integral shown here is equal to the total charge within the volume divided by ϵ_0 .

For a microscopic picture of polarization rather than for the entire material, an analogous equation is used where the molecular polarizability α^* is related to the sum of the polarizabilities of various “ i ” induced polarization types within the material experiencing a local electric field $\mathbf{E}_i(\omega)$. The polarization of individual charges that causes an induced molecular polarization $\mathbf{p}(\omega)$ is written as

$$\mathbf{P}(\omega) = V^{-1} \sum_i \mathbf{p}_i(\omega) = \sum_i [N\alpha \mathbf{E}_i(\omega)]_i \quad 43$$

In Eqn 43, N is the total number of molecules in the volume V . Using this microscopic representation, the local field that is actually felt by all of the bound charges in the system, or molecular dipoles, is defined as the displacement field $\mathbf{D}$ from Eqn. 40c. The relationship between the displacement field and the electric field is $\mathbf{D} = \epsilon^* \epsilon_0 \mathbf{E}$ where $\epsilon^*(\omega) = 1 + \chi^*(\omega)$ is the complex dielectric permittivity. Therefore, it can be concluded that the polarization of the material resulting from the displacement field produced by free charges and the applied electric field is

$$\mathbf{P}(\omega) = \mathbf{D}(\omega) - \epsilon_0 \mathbf{E}(\omega) \quad 44$$

From Eqn. 44, the complex dielectric permittivity ($\epsilon^* = \epsilon' - i\epsilon''$) of a test material between electrodes that form a parallel plate capacitor can be derived by applying Ohms law to the circuit that contains the capacitor. Ohms law states that the complex impedance $Z^*(\omega) = V(\omega)/I(\omega)$ where $V(\omega) = V_0 \sin(\omega t)$ is the voltage applied across the test capacitor with the peak voltage $V_0 = V^+ - V^- = E_0 d \cos\theta$ and d is separation between the electrodes and θ is the angle of the moving free charges. The current through the circuit is given by $I(\omega) = I_0 \sin(\omega t + \psi)$ with the peak current $I_0 = V_0 R^{-1}$ (R is the total resistance of the circuit) which lags the voltage by phase ψ . The $Z^*(\omega)$ that is measured with respect to $V(\omega)$ and $I(\omega)$ is related to the complex dielectric permittivity of the material by

$$\epsilon^*(\omega) = d [i\omega \epsilon_0 A Z^*(\omega)]^{-1} \quad 45$$

where A is the area of the electrode surfaces, as displayed in Figure 16.

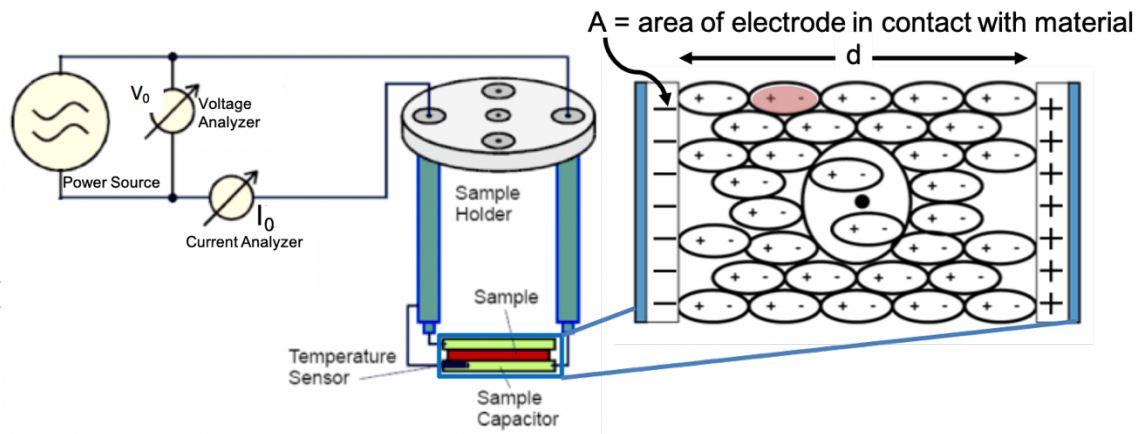


Figure 16: A schematic of a simple dielectric circuit with a sample capacitor (left, adapted from [84]). A cartoon zoom-in on the capacitor (right, adapted from [85]) shows the positive and negative electrodes of area A separated by a distance d . A single dipole, or bound charge, is highlighted in red.

It is important to note that the geometry of the capacitor is important to accurately quantify ϵ^* . This extrinsic property is particular to the density of the dipoles and free charges in the system. The real and imaginary parts of the complex permittivity, ϵ' and ϵ'' , respectively, correspond with the energy stored or lost in the capacitor due to polarizations through the energy density (W_V) of the electric field in Eqn. 46.

$$2W_V = \mathbf{D} \cdot \mathbf{E} = (\epsilon' - i\epsilon'')\epsilon_0 \mathbf{E} \cdot \mathbf{E} \quad 46$$

The relative values of ϵ' and ϵ'' are indicative of the polarization mechanisms and the relative storage or loss of energy within the material due to that polarization. For $\epsilon' > \epsilon''$ there is net energy storage in the polarized materials, and conversely when $\epsilon'' > \epsilon'$ the polarization mechanisms yield a net loss of total energy from the electric field. Another representation of the data from BDS measurements is the complex conductivity, $\sigma^*(\omega) = \sigma' + i\sigma''$, which is related to the complex permittivity by $\sigma^* = i\omega\epsilon_0\epsilon^*$. The conductivity representation of σ' is typically shown for the polarization response of free charges whose motion contributes to energy lost through the relationship with ϵ'' at low frequencies, whereas toward high frequencies the ϵ'' representation of is typically used to observe the polarization response of bound dipoles.

With respect to $\mathbf{P}$ in Eqns. 42, 43 and 44, the polarization of free charges is contained in the dielectric displacement term and the polarization of bound charges is contained in the electric field term. However, different polarization mechanisms occur at different timescales and may contribute linearly to the total complex susceptibility by $\chi^*(\omega) = \sum \alpha_i$ where α is the local polarizability of all of the different "i" polarization mechanisms as shown in Figure 17. First, at fast timescales, achievable by optical frequencies ($\sim 10^{12} - 10^{18}$ Hz), the electronic polarizability α_e is the polarization of the electrons within an atom relative to the nucleus. This polarization is parameterized by the index of refraction $n(\omega)$ which is related to permittivity simply by $n^2(\omega) = \epsilon_\infty$.

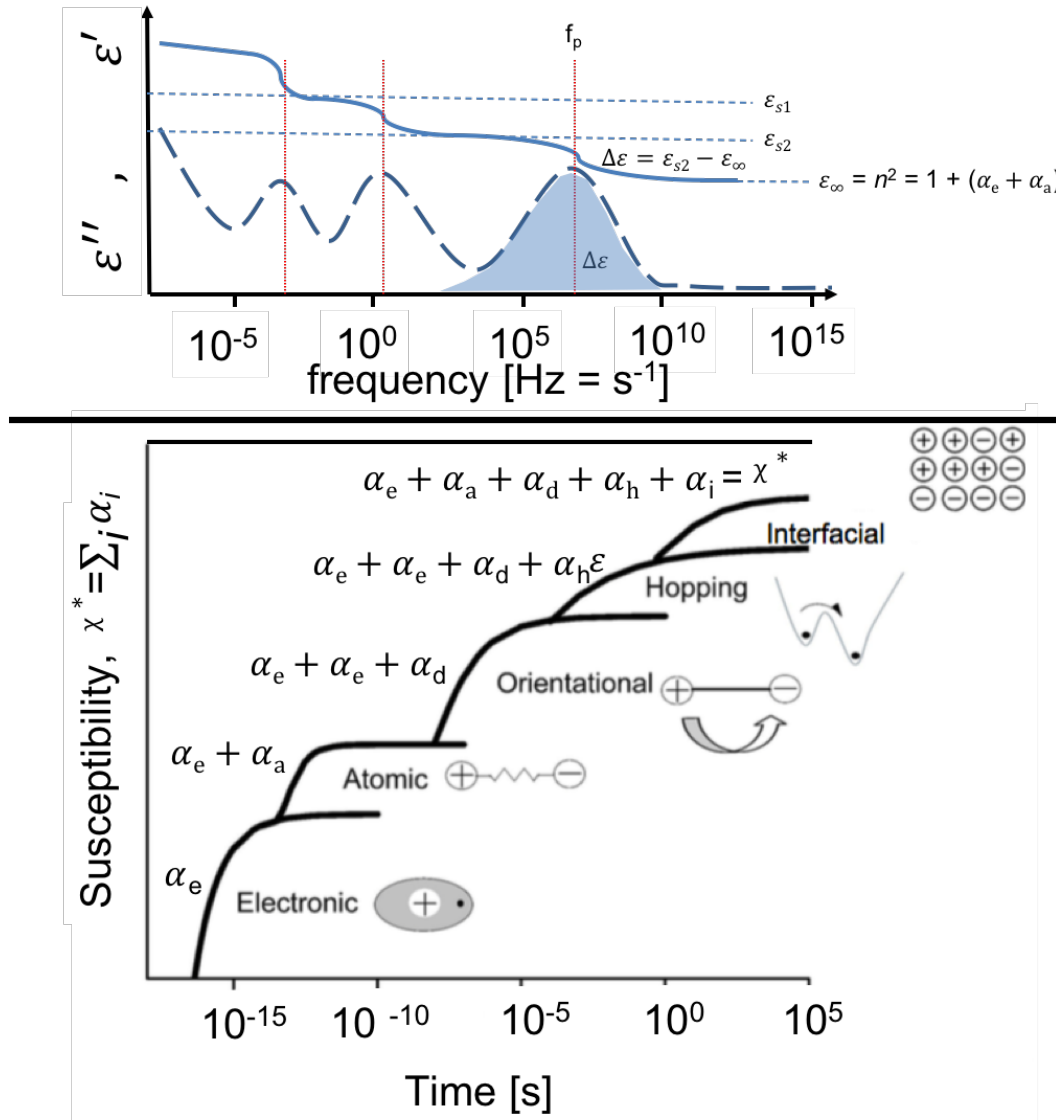


Figure 17: A schematic of the real and imaginary permittivity vs frequency (top) where the characteristic frequency f_p , the dielectric strength $\Delta\epsilon$ and the static permittivity ϵ_{s2} of the slowest relaxation are shown. The dielectric susceptibility of various polarization mechanisms over time and their corresponding polarizabilities are also displayed (bottom).

The ϵ_{∞} term in the refractive index relation is a constant that encompasses the complex permittivity values at high frequencies (often termed resonances at quantized frequencies) and includes electronic polarization but also atomic polarization with polarizability, α_a . Atomic polarization is the cumulative response of atoms within a molecule relative to one another with respect to the electric field ($\sim 10^7 - 10^{12}$ Hz). This polarization causes an induced, non-equilibrium dipole moment within the molecule. For α_e and α_a , these induced polarizations contribute to the overall polarization by $\mathbf{P}_{\infty}$.

These atomic polarizations are in contrast to the next type of polarizations, orientational polarizations which contribute to the overall polarization by $\mathbf{P}_d$. Orientational polarization, with α_d , is the response of the permanent dipole vectors $\boldsymbol{\mu}$ in a molecule whose direction “flips” with respect to the direction of the alternating field (10^{-2} - 10^7 Hz). The next polarization, conductive or ion-hopping polarization with α_h (10^{-2} - 10^4) is the first that involves motions of free charges. This translational hopping of ions contributes to long range diffusion, or dc ionic conductivity which will be discussed toward the end of this section. Finally, at long enough times, these translational hopping processes will cause ions to build up at the electrode surfaces or internal surfaces within the material and is called interfacial polarization with α_i . The responses that are the primary focus of this dissertation are from orientational, conductive and interfacial polarizations. Raman spectroscopy is also used to probe faster vibrational modes associated with atomic and electronic polarization as is discussed later in this chapter.

Thus far, the deviation from equilibrium by various polarization mechanisms have been discussed with respect to the dielectric theory. However, the return of dipoles and free charges to equilibrium, or dielectric relaxation of some polarization response as shown in Figure 18, and the timescales that correspond to these relaxations are the primary interest for the measurements in this dissertation.

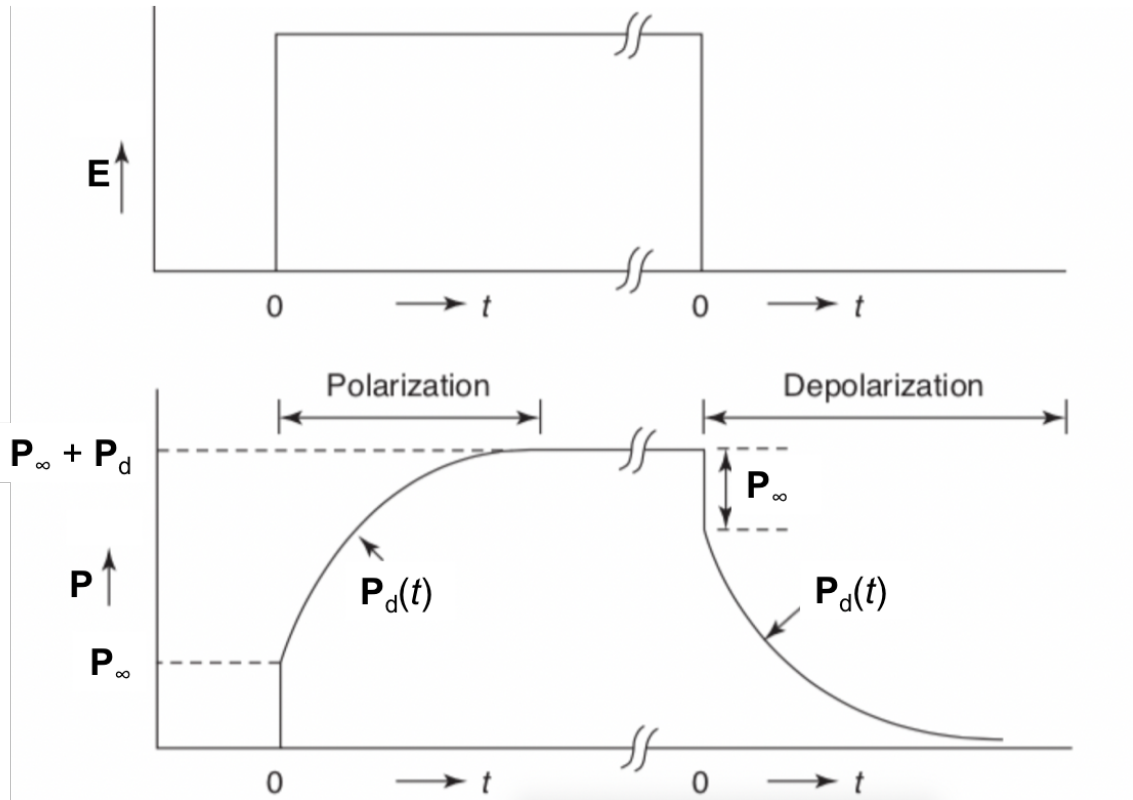


Figure 18: An applied electric field (top) and the polarization response of a material (bottom) vs time. At the instantaneous onset of $E(t)$, the induced polarizations occur for P_∞ then the orientational polarizations occur until reaching a new equilibrium (here by an exponential). When the $E(t)$ is removed the material relaxes back to equilibrium by an exponential process inverse to the polarization response. Figure adapted from [86] with permission

In Chapter 1, relaxations within a material are discussed in the context of the dynamic glass transition, and where a mechanical displacement force is applied to deform a material from equilibrium. Then, when the perturbation is removed or altered, the system takes some time to return to equilibrium. This re-equilibration has some average or characteristic time associated with it as well as some distribution of times that are based on various internal constraints that hamper the mechanism of relaxation. The viscoelastic solid relaxation response in Figure 8 takes a similar shape as the shape of a polarization relaxation in Figure 18.

These polarization relaxations are thermally active motions that result from the force of the applied electric field. With increasing temperature (more internal energy), the frequency of the applied field that is required to displace charges for a certain relaxation to occur decreases (reduced energy needed for polarization). This thermal activation is quantified by some internal friction factor. In this way, the temperature is of particular importance for the relaxation times of various polarization mechanisms. In Figure 19, the reorientation relaxations are shown in the dielectric loss $\epsilon''(f)$ and storage $\epsilon'(f)$ for glycerol, a simple glass forming liquid. In Chapter 1 the dynamics of the glass transition are discussed with respect to some volumetric coordination of molecular motion. As temperature increases, there is a fewer number of molecules required for the coordinated motion, which results in a decrease in the amount of energy required for the relaxation associated with this phenomenon. Therefore, the relaxation associated with the dynamic glass transition becomes slower as temperature decreases.

For orientational polarization, which is the primary focus of this dissertation with respect to relaxations of polymers, the “flipping” of the permanent dipole in response to the forces from the electric field mentioned above is a torsional relaxation mechanism for the dipole vector.

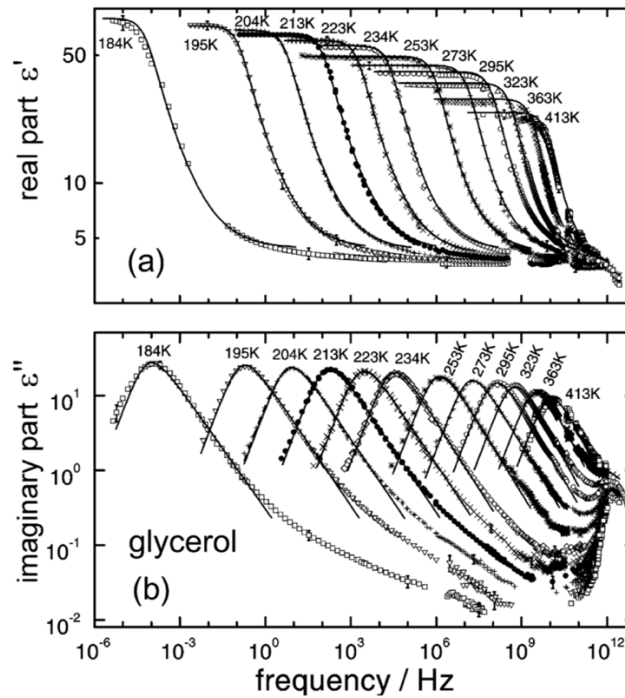


Figure 19: The frequency dependent spectra of dielectric relaxations for glycerol at various temperatures. The primary relaxation observed here slows with decreasing temperature and corresponds to the glassy dynamics of glycerol which for $2\pi f = 10^{-2} \text{ rad s}^{-1}$ defines the T_g . Reproduced from [49] with permission.

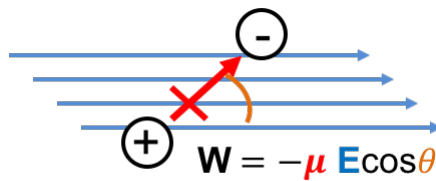


Figure 20: A test dipole μ oriented at an angle θ in a uniform electric field E , and the equation for the interaction energy W associated with the dipole and the field. This is a specific case for Gauss's Law depicted in Fig. 15.

If we consider a single test dipole moment vector $\boldsymbol{\mu}$ among a number N of other randomly oriented dipoles within a volume that have an orientational polarizability α_d , the orientational polarization $\mathbf{P}_d$ of this dipole can be described in an analogous way to Eqn. 43 as

$$\mathbf{P}_d = \sum_k [N\boldsymbol{\mu}]_k \quad 47$$

As mentioned, these relaxations have some distribution of times associate with them whose energy is offset by the internal energy of the system. As depicted in Figure 20 and using Boltzmann statistics, the average orientations of all dipole moments at an angle θ can be described with respect to the direction of a directing $\mathbf{E}_d$ with magnitude $E_{0,d}$ (which excludes the local electric field $\mathbf{E}_l$ produced by the dipole itself, *aka* for a non-interacting dipole)[87].

The average polarized dipole moment $\boldsymbol{\mu}_d$ of magnitude μ with an interaction energy with the field of $W = -\mu E_{0,d} \cos\theta$ follows

$$\boldsymbol{\mu}_d = \frac{\int_0^\pi 2\pi A \sin\theta \mu \cos\theta \exp(\mu E_{0,d} \cos\theta / k_b T) d\theta}{\int_0^\pi 2\pi A \sin\theta \exp(\mu E_{0,d} \cos\theta / k_b T) d\theta} \quad 48$$

where k_b is the Boltzmann constant (1.38×10^{-23} [kg m² K⁻¹ s⁻²]). In the linear regime Eqn. 48 can be simplified to $\boldsymbol{\mu}_d = (\mu/3k_b T) \mathbf{E}_d$, which may be substituted into Eqn. 47 giving

$$\mathbf{P}_d = \sum_k N_k (\mu/3k_b T) \mathbf{E}_d \quad 49$$

Finally, Eqn. 49 for the orientational polarization and Eqn. 43 for the induced polarization ($\therefore \mathbf{P}(\omega) = \mathbf{P}_\infty + \mathbf{P}_d$, where $\mathbf{P}_\infty$ contains atomic and electronic resonance polarizations), along with the relationship between the complex permittivity and susceptibility can all be combined into the total polarization in Eqn 42 to give the fundamental equation for the response of molecular dipoles to an electric field:

$$(\epsilon^* - 1)\epsilon_0 \mathbf{E} = \mathbf{P} \quad 50$$

By employing Eqn. 50, many problems relating to dielectric polarization relaxations can be solved. For example, Onsager developed the relation of Eqn. 51 by more accurately predicting the $\mathbf{E}_i$ for a dipole within a cavity surrounded by a matrix that responds to that dipole's motion. This relation is used to predict the value of ϵ' at low frequencies, ϵ_s following an orientational relaxation relative to the contributions from ϵ_∞ .

$$\epsilon_s - \epsilon_\infty = Fg\epsilon_s n\mu^2(\epsilon_\infty + 2)^2[9k_bT(2\epsilon_s + \epsilon_\infty)]^{-1} \quad 51$$

In the top part of Figure 17, this difference between the ϵ' values at frequencies higher and lower than the relaxation is called the dielectric strength of the relaxation ($\Delta\epsilon = \epsilon_s - \epsilon_\infty$). A consideration for the Lorentz field felt by the dipole due to the polarization of its surroundings was added as the F parameter and used for polymer solutions initially by Stockmayer and Bauer, but was determined to be unity for Type-A polymers by Adachi and Kotaka [65, 88, 89]. An additional consideration by Kirkwood and Fröhlich includes dipoles that correlate in such a way that their initial orientations are not random. This initial orientational anisotropy of dipoles with respect to $\mathbf{E}$ has an effect on the dielectric strength and was added to Eqn 51 to account for this through the Kirkwood-Fröhlich (KF) correlation factor, $g = 1 + \cos\gamma$ where γ is the angle between the test dipole and its nearest neighbors. When $g = 1$ the initial orientations of the relaxing dipoles are random and completely uncoordinated. Using Eqn. 51 that includes the KF correlation factor and a known magnitude of the test dipole moment, the relative preferential alignment of neighboring dipoles can be calculated. The KF correlation factor is heavily considered in Part I of this dissertation for the orientation of chains in block copolymer systems. From relative values of $\Delta\epsilon$, neighboring dipolar orientations that are preferentially aligned parallel to each other correspond to $g > 1$, and for $g < 1$ the dipole orientations are preferentially aligned antiparallel to each other.

Another problem that employs Eqn. 50 was solved by Debye, who considered the relaxation mechanism of a non-interacting dipole in response to the

time dependent field to have an exponential form.[87] From the theory above, this model by Debye returns

$$\epsilon^* = \epsilon_\infty + \Delta\epsilon(1+i\omega\tau)^{-1} = \epsilon_\infty + \Delta\epsilon(1-i\omega\tau)(1+\omega^2\tau^2)^{-1} \quad 52$$

Other models, like the Cole-Cole or Cole-Davidson relaxations, consider the dipole response to have a stretched exponential form accounting for symmetric or asymmetric stretching, respectively. A combination of these two models was suggested by Havriliak and Negami to match relaxations from dielectric experiments using Eqn 53 called the Havriliak-Negami (HN) function

$$\epsilon^* = \epsilon_\infty + \Delta\epsilon_{HN}(1+(i\omega\tau)^\alpha)^{-\gamma} \quad 53$$

This is particularly useful for describing a single relaxation process measured by BDS rather than using a linear superposition of multiple Debye relaxations or modes that sum to form cooperative motions of a single relaxation with a weight on a particular mode, as in the relaxation of a Rouse chain, or any polymer chain for that matter. This superposition of Debye relaxations is given by

$$(\epsilon^* - \epsilon_\infty)\Delta\epsilon^{-1} = \sum_{\tau=0}^N g_p[\ln \tau (1+i\omega\tau)^{-1}] \quad 54$$

where g_p is a the intensity of a mode or more specifically a weighting function that is based on the α and γ parameters from Eqn. 53. It is worth noting that Eqn. 54 is very similar to the normal modes experimentally determined for PI in Eqn. 39a in Chapter 1. For the Type-A homopolymer chain, the τ_1 mode dominates the dielectric spectrum at longer times with faster modes having a relatively reduced weight. As the size of the chain increases, CR and DTD mechanisms begin to influence the relaxation and faster modes have more weight with respect to Eqns. 54 or 39a. This theory was also combined with explanations from experimental results by Likhtman, McLeish and others to incorporate solutions to Eqn. 21 in the Tube model to account for Rouse modes of subchains without full reptation of the

chain [37, 68]. Finally, the peak frequency or frequency of maximum loss of a dielectric process modeled by a single HN function is related to α and γ as well using

$$\omega_p = \tau_{HN}^{-1} [\sin(\alpha\pi/(2+2\gamma))]^{1/\alpha} [\sin(\alpha\gamma\pi/(2+2\gamma))]^{-1/\alpha} \quad 55$$

and the dielectric strength of a relaxation process is $\Delta\epsilon_{HN}$.

The relationship between the real and imaginary parts of the dielectric function, the Kramers/Kronig relations, are used by a Hilbert transform ($H[x] = 2\pi^{-1} \int x/(t-\tau) d\tau$):

$$\epsilon'(\omega) - \epsilon_\infty = H[\epsilon''(\omega)] \quad \text{or} \quad \epsilon''(\omega) = H[\epsilon'(\omega) - \epsilon_\infty] \quad 56$$

This is a particularly useful transformation considering that the same information regarding relaxation processes is contained in both ϵ' and ϵ'' . As stated before, there is a relationship between σ' and ϵ'' ($\sigma' = \omega\epsilon_\infty\epsilon''$). This can result in spectral characteristics from slower relaxations of μ_d with weak dielectric strengths to be hidden beneath the strong polarization if ions in ϵ'' . Since this connection is not direct for ϵ' , Eqn. 56 can give a representation of ϵ'' without ionic polarization by $\epsilon''_{der} = -\pi/2[\partial\epsilon'/\partial\ln(\omega)]$. Additionally, the dielectric strength for a relaxation in ϵ'' can be determined from Eqn. 56 without directly knowing ϵ_s or ϵ_∞ by $\Delta\epsilon = 2\pi^{-1} \int \epsilon''(\omega) d\ln\omega$.

As stated in Chapter 1 for the fluctuation dissipation theorem, relaxations from small perturbations may be considered equivalent to random equilibrium fluctuations. These equilibrium fluctuations are contained in the correlation function $\Phi(t)$ in the time domain from Eqn. 36, and is related to the frequency dependent dielectric function $\epsilon^*(\omega)$ by

$$(\epsilon^* - \epsilon_\infty)\Delta\epsilon^{-1} = - \int_0^\infty \frac{d}{dt} \Phi(t) e^{-i2\pi f t} dt \quad 57$$

The correlation function is directly proportional to the normalized autocorrelation function of the orientational polarization response by $\Phi(t) = \frac{\langle \mathbf{P}_d(t) \cdot \mathbf{P}_d(0) \rangle}{\langle \mathbf{P}_d^2(0) \rangle}$. According to Stockmayer's classification of polymers dipoles, for a polymer chain with monomeric dipole moments within the polymer backbone that can be decomposed into components that are aligned perpendicular ($\mu^\perp$, type-B) and parallel ($\mu^\parallel$, type-A) to the chain contour, when $n \geq 10$ (where n is the number of segments in the polymer chain) the timescales of chain and segmental orientational polarization relaxations become well-separated in the time domain [89-91]. This allows the total orientational polarizations of the Type-AB chains to be mathematically defined as a sum of individual contributions from the monomeric segmental relaxations and the chain normal mode relaxations[46]. Therefore, the normalized autocorrelation function between the polarized dipoles of the n^{th} and m^{th} segmental dipoles in chain "i" can be related to the orientation polarization of the polymer material using Eqn. 47 through the following equation:

$$\frac{\langle \mathbf{P}_d(t) \cdot \mathbf{P}_d(0) \rangle}{\langle \mathbf{P}_d^2(0) \rangle} = \sum_i \frac{\sum_n \sum_m \langle \mu_i^\parallel(n;0) \cdot \mu_i^\parallel(m;t) \rangle + \sum_n \sum_m \langle \mu_i^\perp(n;0) \cdot \mu_i^\perp(m;t) \rangle}{\sum_n \sum_m \langle \mu_i^\parallel(n;0) \cdot \mu_i^\parallel(m;0) \rangle + \sum_n \sum_m \langle \mu_i^\perp(n;0) \cdot \mu_i^\perp(m;0) \rangle} \quad 58$$

Furthermore, by summing all of the contributions of parallel components of monomeric dipoles ($\mu^\parallel$) in $\Phi(t)$ over all segments, we obtain an expression for the end-to-end dipole vector fluctuation of the Type-A probe chain that does not contain any dipole inversions along the chain contour, $\mathbf{R}_i(t)$, in the form of an autocorrelation function:

$$\sum_n \sum_m \frac{\langle \mu_i^\parallel(n;0) \cdot \mu_i^\parallel(m;t) \rangle}{\langle \mu_i^\parallel(n;0) \cdot \mu_i^\parallel(m;0) \rangle} = \frac{\langle \mathbf{R}_i(t) \cdot \mathbf{R}_i(0) \rangle}{\langle [\mathbf{R}_i(0)]^2 \rangle} \quad 59$$

Notably, cross-correlations in the *polarization* function of monomeric dipoles within a single chain and neighboring chains of a Type-AB polymer in response to $\mathbf{E}$ have been shown experimentally to be negligible due to low interaction energies between the dipoles compared to the thermal motion of the segments[92].

However, as was seen in Chapter 1, cross-correlations in the *local correlation* function $C(t)$ for may not be negligible. Thus, cross-term contributions from $C(t)$ may contribute to the orientational polarization response $\Phi(t)$ due to coordinated motions of the polymer segments and chains from Eqn. 36 in Chapter 1. Analytically, these cross-terms have historically been considered in the $\Delta\epsilon$ term through the g parameter in Eqn. 51 and will be considered in more detail in Part I. Historically, the normal modes of a chain have been used interchangeably with the dielectric relaxation of the chain end to end dipoles. However, the mathematical normal modes determined through the $C(t)$ reflected by measuring ϵ^* through Eqns. 57-59 can be misleading due to various thermodynamic discussed in Ch. 3. Therefore, the dielectric response of the chain end-to-end dipole fluctuations are termed the “chain relaxation” in this dissertation in order to keep experimental findings separate from mathematical considerations of coupled harmonic oscillations of chain segments which will be termed the “normal modes”.

From Equations 57-59 and Equations 23 and 36, the chain end-to-end dipole fluctuations (chain relaxation) in relation to the normal modes of the polymer chain are realized in the complex dielectric function of a Type-A polymer chain, and allows inferences to be made about the effects of the various constraints on the polymer chain dynamics[93]. Particular constraints, some of which were summarized in the last part of Chapter 1 for homopolymers and constraints for block copolymers are detailed in the introduction to Chapter 3, can change the characteristic relaxation times/frequencies as determined by a peak in the dielectric loss. However, since these relaxations are not quantized at a single frequency and often are described by a stretched exponential distribution of relaxation times, it is often the case that various constraints lead to an alteration in relaxation time distributions and/or characteristic relaxation times. Eqn. 60 gives the relationship between the relaxation time distribution function $L(t)$ and the complex dielectric function. For relaxations that can be easily modeled by Eqns. 53 or 54, the $L(t)$ is realized quite easily. However, various numerical methods

have been considered for model-free realizations of $L(t)$ with differing degrees of success [94-96]. The shape of a dielectric relaxation in the ϵ'' spectrum corresponds to the distribution of relaxation times from Eqn. 60 which may change due to various constraints. Ultimately, identifying how the changes in dielectric normal mode chain relaxation spectral shape relates to constraints to the polymer motion, particularly branching in block copolymers, is the goal of this dissertation

$$\epsilon^* - \epsilon_\infty = \Delta\epsilon - \int_{-\infty}^{\infty} L(t) (1+i\omega t)^{-1} dt \quad 60$$

Finally, to return to Maxwell's equation in Eqns. 40, the current density is related to the applied electric field by $\mathbf{j}(\omega) = \sigma^*(\omega)\mathbf{E}(\omega)$ where the complex conductivity is the linear coefficient between the current $\mathbf{j}$ and the electric field $\mathbf{E}$ for a specific material in a capacitor. As stated earlier, σ^* is directly related to ϵ^* and is often used to represent dielectric data for the slower ion-hopping or interfacial polarizations and to characterize ion transport in electrolyte systems. This will become particularly important in Chapter 8 of this dissertation when the conductivities of a special class of ion containing polymers are analytically parsed to reveal the effect of ion transport in nanoconfined systems.

X-ray Scattering

The foundations of all X-ray scattering methods (e.g. wide-angle, small-angle, grazing-incidence, etc.) begin with similar physics as the other methods in this dissertation of electromagnetic radiation interacting with matter. The interaction of the monochromatic incident x-ray beam (wavelength, λ , in the nanometer regime, $10^{-2} - 10^1 \text{ nm}$) with a system that has some molecular order results in a scattering or diffraction profile based on the geometry and length-scale of the order. The ordered atoms and/or molecules act as narrow apertures that cause diffraction of the incident beam based on the same physics of the fundamental laser diffraction grating experiments that follow the Huygens-Fresnel principle. The wavelength of the incident beam scatters elastically off of the electron clouds that exist between

nuclei with a characteristic spacing length d . The relative density change of the electrons causes the incident radiation at vector $\mathbf{k}_0$ to scatter at an angle 2θ at a new vector $\mathbf{k}_s$ (see Fig. 21). As the length scale of the atomic or molecular order d increases, 2θ decreases. A 2D photon detector beyond the sample measures higher densities of scattered photons based on regular order in the material. These atomic/molecular spacings, the angle between the incident and scattered vectors and x-ray wavelength are related by Bragg's Law $\lambda = 2d \sin\theta$.

The intensity of the scattering measured by the detector I is related to the scattering vector $\mathbf{q} = \mathbf{k}_0 - \mathbf{k}_s$ with magnitude $q\lambda = 4\pi \sin\theta$ by

$$I(\mathbf{q}) = \int \rho(\mathbf{x}) \exp(-i\mathbf{q} \cdot \mathbf{x}) d\mathbf{x} \quad 61$$

where $\rho(\mathbf{x})$ is the local electron density at a point in the sample represented by the vector $\mathbf{x}$. Changes in this electron density cause a change in the refractive index for the incident x-rays which ultimately causes them to scatter. When these electron density changes exist at regular intervals a pattern in that scatter can be measured. From Bragg's law and the magnitude of the scattering vector q , the real space distance of the diffraction spacings of the scattering centers is calculated by $d = 2\pi q^{-1}$. For very small d the scattering vector $\mathbf{q}$ will be large (*i.e.* wide-angle) such that measurement requires the sample detector distance (shown in Fig. 21) to be very small. Conversely, for larger length-scale scattering centers such as in phase separated block copolymers the $\mathbf{q}$ will be small (*i.e.* small-angle) requiring large sample detector distances.

Figure 22 shows various scattering vector peaks and their relative locations normalized by the lowest q value peak, termed the Bragg peak q^* . These different profiles are associated with different geometries of block copolymer phase separated morphologies (introduced in detail in Part I) by small-angle x-ray scattering (SAXS) and employed by the experimental investigations in the first part of this dissertation.

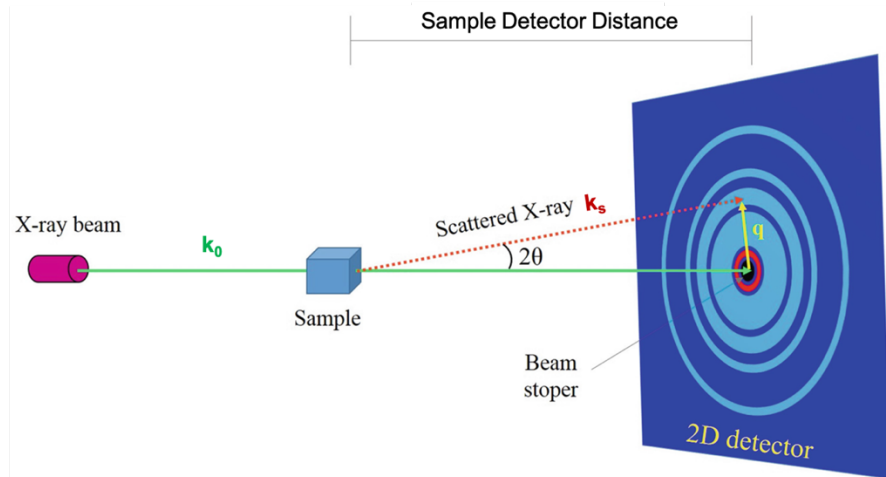


Figure 21: Schematic of X-ray scattering. The incident beam of wavelength λ scatters off of a sample creating a diffraction pattern on a 2D detector. The measured scattering vector $q = k_0 - k_s$ represents a vector space lengthscale in real space by $d = 2\pi q^{-1}$ where d is the distance between the ordered molecules or atoms that act as diffraction gratings in the sample. The light blue circles are the high density of scattered x-rays which are typically integrated to give a 1D profile. Adapted from [97] with permission.

A) Peak positions (expressed as q/q^*) of Bragg reflections for various structures

Structure	Ratio q/q^*
Lam	1, 2, 3, 4, 5, 6,...
Hex ($p6mm$)	1, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, $\sqrt{12}$, ...
BCC ($Im\bar{3}m$)	1, $\sqrt{2}$, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{5}$, $\sqrt{6}$, ...
FCC ($Fm\bar{3}m$)	1, $\sqrt{4/3}$, $\sqrt{8/3}$, $\sqrt{11/3}$, $\sqrt{12/3}$, $\sqrt{16/3}$, ...
Gyr ($Ia\bar{3}d$)	1, $\sqrt{4/3}$, $\sqrt{7/3}$, $\sqrt{8/3}$, $\sqrt{10/3}$, $\sqrt{11/3}$, ...

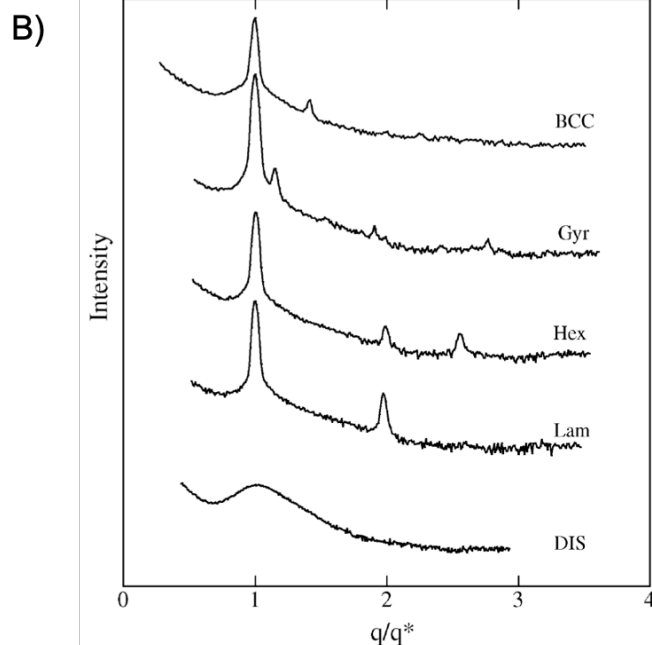


Figure 22: Table of SAXS peak positions at q values relative to the Bragg peak for block copolymer morphologies (A) and the representative 1D scattering profiles that correspond to these structures (B). Both are reproduced from [98] with permission.

At higher q values in the scattering profile, which corresponds to shorter sample detector distances, the spacings of atoms are measured with relatively broad peaks for amorphous structures and sharp peaks are measured for ordered crystalline lattices. Many studies specifically study the structure factor of the elastic scattering in x-ray scattering experiments, while other associate specific distances of the phase separation to different properties of the system. The primary use of SAXS in this dissertation is to measure domain sizes and spacings, along with confirmation of the morphology expected upon phase separation. Wide-angle X-ray scattering measurements were also performed in combination with SAXS, but the data are minimally used in this dissertation. Transmission electron microscopy was performed as a supplemental tool to confirm the geometries of the morphological structure.

Transmission Electron Microscopy

The wave-particle nature of electrons gives transmission electron microscopy (TEM) a unique photographic characteristic to this microscopy without the use of a specific type of radiation. The De Broglie wavelength of the electrons λ is far smaller than for visible light, and therefore, from $d = \lambda (2n \sin \alpha)^{-1}$ being the resolution of an image with n as the refractive index of the lens and α as the lens cone-angle, the possible magnification of an image using electrons is much greater than for traditional light microscopy. This technique focuses a beam of electrons from a tungsten filament cathode onto a thinly sliced or film prepared sample. Rather than a typical lens, a solenoid coil creates a uniform magnetic field to focus the electrons onto the sample by changing the current through the coil.

Electrons from the focused beam are absorbed or scattered by large or high-density atoms in the thinly sliced sample, and pass through smaller lower density atomic structures. The transmitted electrons are collected and developed in a similar way to a classical photograph to reveal an image of the material.

The particular use of TEM in this dissertation is as a supporting technique to confirm the particular microstructure of phase separated block copolymers. The polymers in this dissertation are primarily long-chain carbon-based structures, and therefore, require stains solvated into a particular polymer type or block with heavy atoms such as Osmium (Os). The selective uptake of fumes from OsO_4 solution into a polymer block will then negatively-contrast the different polymer phases in the sample when imaged with TEM. The bulk ($\sim 100\mu\text{m}$ thick) block copolymer materials in Part I of this dissertation needed to be thinly sliced to be measured by TEM required. Bulk samples were sliced to $\sim 100\text{nm}$ by the relatively common technique of cryo-ultramicrotomy. More experimental details are given in the respective chapters in which TEM is used.

Raman Spectroscopy

Raman spectroscopy is a type of vibrational spectroscopy that relies on a specific type of inelastic scattering of monochromatic light by a material. The energy of the light is partially absorbed causing electrons in the sample to increase in energy into an excited virtual state. Some of the energy from this absorbed light is dissipated by vibrational modes of molecular bonds between atoms, and when the excited electrons that form these bonds relax back to their equilibrium ground state emitting photons of lower frequency than the light used to excite them this is called Stokes Raman scattering. When the vibrational mode transfers energy to the photon rather than dissipating it, causing the scattered light to have a higher frequency than the incident beam it is called anti-Stokes Raman Scattering. See Figure 23 for a visualization of this inelastic scattering.

These excitation and re-emission mechanisms that result in Raman scattering are statistically rare but occur frequently enough to measure the relative shift in energy of the scattered light from that based on the frequency of the monochromatic excitation. Different bond types (molecular, intermolecular, etc.) and different bond conformations (*trans*, *gauche*, etc.) result in different shifts frequency based on the energy quantized by the vibrational mode. This is in contrast to the more widely used vibrational spectroscopy technique of Fourier transform infrared spectroscopy (FTIR) which irradiates a sample with infrared light of a relatively wide frequency range and measures the relative amount of this light transmitted through the sample at frequencies within that range. Both techniques result in measurement of modes of bond vibrations like those in Figure 23. Fundamentally, these vibrational modes cause small but quantized changes in the electronic polarizability of the electrons that make up a bond (see discussion of Eqns. 42-44). However, the frequencies of the modes that are measured are limited by the frequency range of the incident light and the detector in FTIR, whereas any virtual state that occurs using the particular laser employed can be measured by Raman and is only limited by the detector. Raman spectroscopy is only used in the final chapter of this dissertation but is relied upon for a substantial portion of that study.

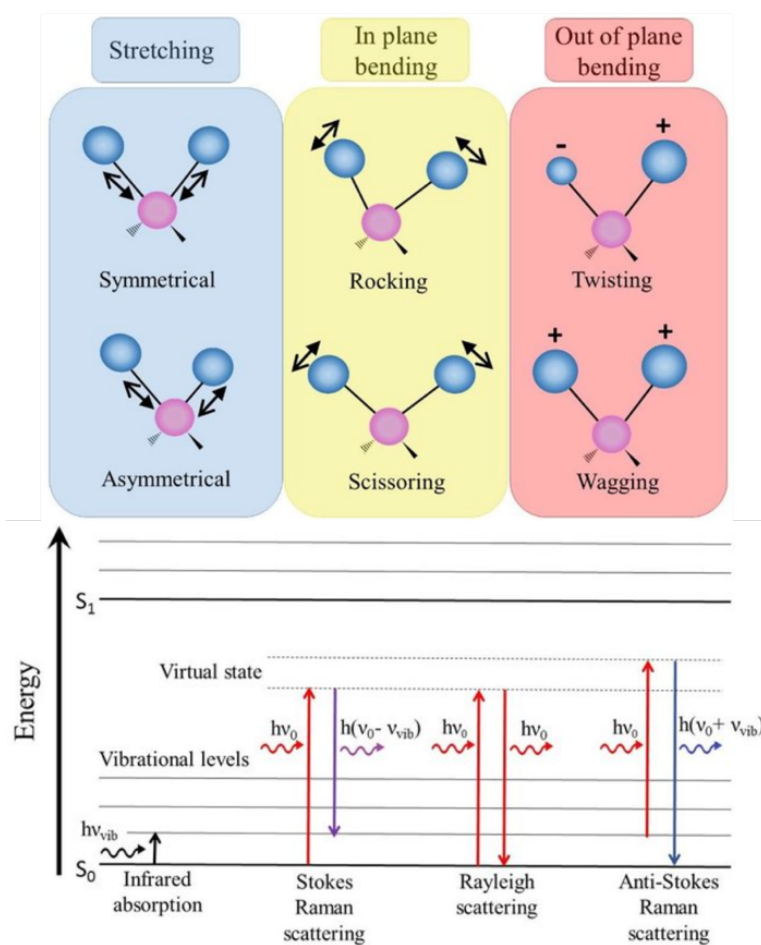


Figure 23: The modes of bond stretching and bending measured by vibrational spectroscopy (top) and the mechanisms of excitation and possible re-emission of light for FTIR and Raman spectroscopies (bottom). Images are reproduced from [99].

PART I: Block Copolymer Architecture

Introduction

Part I of this dissertation reviews the literature of block copolymer thermodynamics and the dynamics of the polymer chains that make them up, then presents original experimental evidence of changes in dynamics by the dielectric relaxation spectra due to systematically varied branching chain architectures within the context of the literature presented. Due to constant advances in polymer synthesis, the connectivity of various polymer chains has become almost limitless. While the synthesis methods of these types of polymers are widely covered in the literature, the properties and motions of block copolymers have become completely separate research foci. We by defining block copolymers (BCPs) as two or more homopolymers of different chemistries that are covalently connected by one or more junction points. The simplest molecular architecture of BCPs is the AB linear diblock which connects one end of homopolymer A to one end of homopolymer B. From here, a third block C can be added at either end of the AB linear diblock (to the A end or B end) to create a linear ABC triblock copolymer. The configurations of blocks (ABC ACB or BAC) change the characteristics of the resulting material. Rather than a third block C, a third block of A or B can be added to produce ABA (or BAB) linear triblock copolymers. The ABA molecular architecture and chain configuration is the prototypical thermoplastic elastomer when block A has a low T_g giving rigidity and strength to the material while the low T_g B block gives rubbery elasticity to the material. The differences in T_g are only achieved when the two blocks do not mix which causes self-assembled microphase separation. Similar to oil and water being immiscible causing macroscale phase separation, when the blocks of a BCP do not mix, their interaction energies are such that they avoid each other and form distinct phases with many different geometries. This is based on the energy mixing for the system based on different contributions to the free energy of the system.

The free energy of a blended system is governed by the counter-balance between enthalpy and entropy by basic thermodynamics principles ($dU = dH - PdV$

- VdP , $dG = dH - TdS - SdT$, where H is enthalpy, U is internal energy, G is the Gibbs free energy, PVT are pressure volume and temperature and S is entropy). For an isothermal and incompressible system ($dT = 0$ and $dV = 0$), a minimum in the free energy, $dG = dU - TdS$ determines stability in the equilibrium state of some particular geometry for the phase separation of the BCP system. The enthalpy of mixing H_m (the primary internal energy term) is the driving force for phase separated blends of homopolymers. However, when polymer chains are covalently bound at a junction point for a BCP system, the enthalpy term is offset by additional energetic terms, namely chain stretching energy E_s which is calculated through the conformational entropy of the chain (see Chapter 1 for details on energy associated with chain conformational entropy). The Flory-Huggins theory for polymer blends characterizes the enthalpy of mixing using χ_{AB} as a parameter for mixing energies

$$\chi_{AB} = (k_b T)^{-1} [\epsilon_{AB} - (1/2)(\epsilon_{AA} + \epsilon_{BB})] \quad 62$$

where ϵ_{ij} is the interaction energy between i and j segment types by [14, 100]

$$\epsilon_{ij} = -\sum_{i,j} \frac{3}{4} [I_i I_j / (I_i + I_j)] [\alpha_i \alpha_j b^{-6}] \quad 63$$

In Eqn 63, I is the ionization potential and α is the segment polarizability. For $\chi_{AB} > 0$ the average interaction energy of any monomer with like monomers is less than the interaction energy of unlike monomers, and the system drives to minimize this energy and therefore phase separation occurs. Conversely for $\chi_{AB} < 0$ the two blocks will blend. In this simplistic description of Flory-Huggins solution theory, the extent of phase separation increases with total number of segments ' n ' and decreases with temperature as per the free energy of a Gaussian chain which accounts for the entropic chain stretching. It is noteworthy here that below the T_g of one of the blocks, an equilibrium state may be quasi-stable due to limited mobility of segmental relaxations, and it is important that when considering the dynamics in an equilibrium state, that the free energy is minimized, and the system is not simply quasi-stable.

From the thermodynamics above and Eqns. 62 and 63, the total change in the Gibbs free energy for mixing two homopolymers ($\Delta G_m = \Delta H_m - T\Delta S_m$), with volume fractions of each homopolymer given by ϕ_A or ϕ_B (where $\phi_A + \phi_B = 1$) and number of segments in each block n_A or n_B , results in

$$\Delta G_m = k_b T [n_A^{-1} \phi_A \ln \phi_A + n_B^{-1} \phi_B \ln \phi_B + \phi_A \phi_B \chi_{AB}] \quad 64$$

This is a simple model that has been expanded upon to also consider covalently joining the two blocks together. This idea is central to but exists in a modified form for self-consistent field theory (SCFT). SCFT is a mean field theory that accounts for local interaction potentials among neighboring segments while also accounting for the entropic considerations of the Gaussian chain model in Chapter 1. Figure 24 shows a typical phase diagram for an AB block copolymer with representative morphologies at various block fractions. The phase diagram displays the morphology of minimized ΔG_m in Eqn. 64 plotted for χn as ϕ_A or ϕ_B changes for a diblock copolymer system. In the following chapter SCFT is summarized from the descriptions by Matsen with a specific focus on deriving terms that are useful when considering the relaxations of polymer in BCP systems [101, 102]. Additional complexity arises when branching architectures are introduced. While these aspects of phase separation are not the primary focus concentration of this dissertation, they must be considered in detail because, as will be seen, the dynamics measured by dielectric spectroscopy are altered by different geometries and chain connectivity.

Outline

In the introduction to Part I above, the fundamentals of block copolymer phase separation are laid out. Next, these fundamentals are expanded upon and the resulting energies of chain stretching, and the interface are derived, and the dielectric relaxation of PI in linear block copolymers from the literature are discussed in the context of the current state of the field. From this discussion, the

following three chapters expand on the dynamics of block copolymers with non-linear architectures, specifically the miktoarm star copolymer.

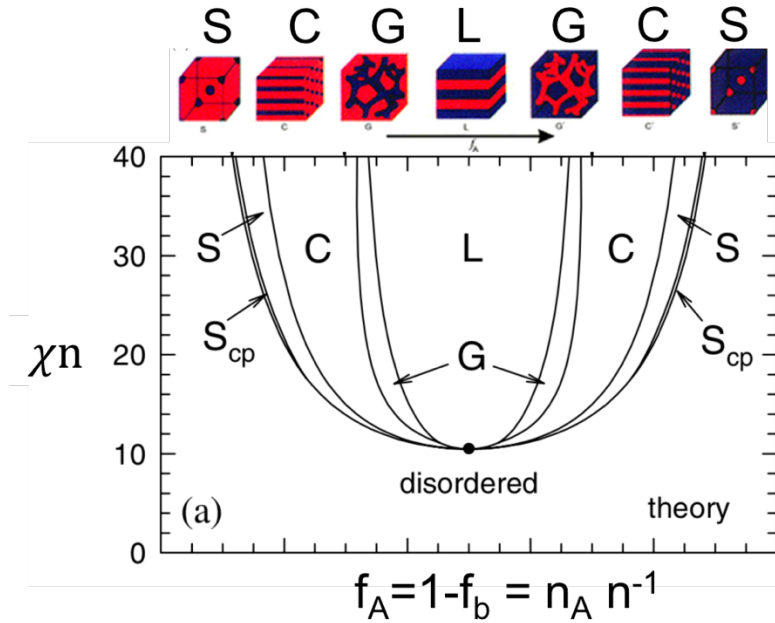


Figure 24: A standard block copolymer phase diagram of the product of Flory Huggins interaction parameter with the number of segments in the block copolymer plotted against the fraction of the A component. Adapted from [103, 104] with permissions.

The materials in Chapters 3-6 include four linear diblock copolymers of poly(*cis*-1,4-isoprene)-*b*-(2-vinylpyridine) (PI-P2VP), three ABC miktoarm star copolymers of poly(styrene)-(*cis*-1,4-isoprene)-(2-vinylpyridine) (PSPIP2VP), three 3-arm AB₂ miktoarm star copolymers of poly(styrene)-(*cis*-1,4-isoprene)₂ (PS-PI₂), three 4-arm A₂B₂ miktoarm star copolymers of poly(styrene)₂-(*cis*-1,4-isoprene)₂ (PS₂-PI₂) and one 3-arm A(B-A')₂ miktoarm star copolymer of poly(styrene)-(*cis*-1,4-isoprene – *b* – styrene')₂ (PS-(PI-PS')₂) which has smaller PS' blocks terminating the PI chains making this miktoarm polymer similar to a triblock system.

Chapter 3 is separated into two sections: First, the theory of phase separation by self-consistent mean field theory (SCFT) is detailed; second, the dielectric relaxations of the linear PS-PI diblock copolymers are reviewed from the literature with a meta-analysis of the normal modes of PI. The results from this meta-analysis lays a foundation for considering the effects of branched miktoarm architectures on the PI dielectric relaxations in the Chapters 4-6.

In Chapter 4, four PI-P2VP systems are studied to determine the effect of the P2VP block on the dielectric PI chain relaxation compared to the well-studied PS-PI systems from the literature. The molecular weight characteristics for these polymers are found in Table 1 with the gel permeation chromatography (GPC) peaks shown in Figure 25 which are compared against polystyrene standards. The PI-P2VP systems in Chapter 4 are investigated in order to then incorporate the poly(2-vinylpyridine) block as a third arm to PS-PI systems to form the ABC miktoarm star architecture. The characteristics of the PSPIP2VP systems are also found in Table 1. All of these polymers were synthesized by scientists at the Center for Nanophase Materials Science at Oak Ridge National Laboratory.

In Chapter 5, two of the A_nB_m miktoarm star diblock copolymers (PS₂PI₂ and PSPI₂) that form lamellar morphology are investigated to determine how the connectivity of the blocks and the relative number of arms influence the PI chain relaxation. In Chapter 6, the remaining A_nB_m polymers are studied to determine how different morphologies and molecular weights change the PI dynamics in the

architecturally asymmetric PS-PI₂ polymers while also comparing the dynamics of the PS-(PI-PS')₂ polymer. There are seven total polymers in the studies covered in Chapters 5 and 6, and their characteristics and available GPC chromatograms are shown in Table 2 (same as Table 9) and Figure 26, respectively. Studying these molecular architectures and determining how they influence the dielectric chain relaxation develops a full fundamental realization of the dynamics in phase separated block copolymer systems. These polymers were also synthesized by CNMS scientists.

Table 1: Polymer characteristics for Chapter 3

Sample ID	Total Molecular Weight			PI Block			P2VP Block		w% of P2VP	
	M _n	M _w	PDI	M _n	M _w	PDI	M _n	M _w	GPC	NMR
20kPI-5kP2VP	23,200	24,800	1.07	19,000	20,000	1.05	4,200	4,800	18.0%	12.2%
20kPI-10kP2VP	31,600	33,500	1.06				12,600	13,500	39.9%	32.1%
20kPI-15kP2VP	35,700	38,200	1.07				16,700	18,200	46.8%	40.0%
20kPI-20kP2VP	40,600	43,800	1.08				21,600	23,800	53.2%	42.0%
	M _n of Blocks (x10 ³ NMR)			Volume fraction ratios						
Sample ID	PS	PI	P2VP	ϕ_{PS}/ϕ_{PS}	ϕ_{PI}/ϕ_{PS}	ϕ_{P2VP}/ϕ_{PS}	$[X] = \phi_{P2VP}/\phi_{PI}$	PDI	Densities for ϕ (g/cm ³)	
10kPI-10kPS-18kP2VP	10		18	1	1.18	1.79	1.4	1.07	PS	1.05
10kPI-10kPS-35kP2VP			35			3.3	2.8	1.09	PI	0.91
10kPI-10kPS-48kP2VP			48			4.5	3.8	1.12	P2VP	0.97

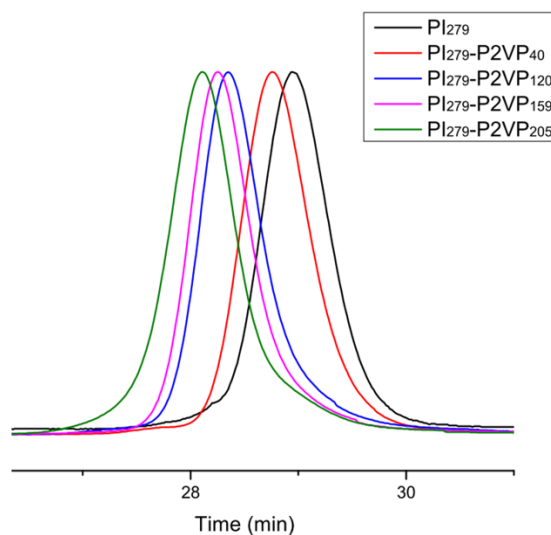


Figure 25: GPC chromatograms of the homopolymer PI precursor and of the linear PI-P2VP diblock copolymers. P2VP40 = 5k, P2VP120 = 10k, P2VP59 = 15k and P2VP205 = 20k. The synthetic chemist who produced these polymers did not provide specific GPC or NMR data for the PSPIP2VP miktoarm samples. See Table 1 for the characteristics of these polymers.

Table 2: Characteristics of polymers for Chapters 4 and 5

Architecture ID	Sample ID	Molecular weight (kg/mol)					ϕ_{PI}^a	$\bar{D}$
		$M_{wPS,arm}$	$M_{wPS,block}$	$M_{wPI,arm}$	$M_{wPI,block}$	$M_{wPS'arm}$		
$PSPI_2$	18k-10k ₂	18	18	10	20	--	0.565	1.05
	18k-18k ₂	18	18	18	36	--	0.7	1.02
	18k-32k ₂	18	18	32	64	--	0.806	1.01
PS_2PI_2	16k ₂ -9k ₂	16	32	9	18	--	0.396	1.04
	16k ₂ -24k ₂	16	32	24	48	--	0.636	1.01
	16k ₂ -52k ₂	16	32	52	104	--	0.791	1.08
$PS(PI-PS')_2$	18k(12k-3k') ₂	18	24	12	24	3	0.538	1.06

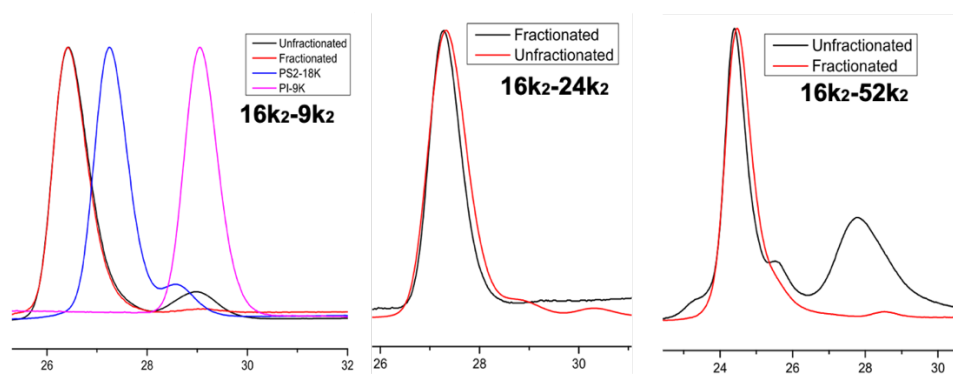


Figure 26: GPC chromatograms of the PS_2PI_2 polymers with the homopolymer PS_2 precursor (blue, left plot) and PI precursor (pink, left plot) for the 16k₂9k₂ polymer, along with the fractionated (red) and unfractionated (black) chromatograms for the 16k₂24k₂ polymer (center) and 16k₂52k₂ polymer (right). The synthetic chemist who produced these polymers did not provide specific GPC or NMR data for the remaining polymers from Table 2.

Chapter 3: Self-Assembly and Dynamics of Block Copolymers

A version of the second section of this chapter, “Block Copolymers: Dynamics” will be published as a meta-analysis review paper by Thomas Kinsey, Emannuael Mapesa and Joshua Sangoro in Physical Review Materials:

Kinsey, *et. al.* *The spectral shape of the polyisoprene dielectric normal modes in phase separated diblock copolymers.* PRMaterials, 2021

The analysis of the literature data and writing of this paper was performed by TK. EUM and JR edited and revised the content, and JR provided financial support.

This chapter is separated into two sections. The first covers the state of the art in the theory for predicting morphologies of phase separated block copolymers, primarily linear diblock copolymers, using thermodynamics. The information in this first section (Block Copolymers: Self Assembly) is also found in several peer reviewed articles and texts, and exists here as a summary with a focus on the various aspects of the field theory that may inform the dynamics of the segments and chains in block copolymers. The second section covers the chain dynamics (*i.e.* dielectric normal mode) of phase separated diblock copolymers as measured by dielectric spectroscopy. This section (Block Copolymers: Dynamics) details the best practices for analyzing these types of data and what to expect for the dielectric relaxation shapes of PI in different morphological phases. The information in the second section is original to this dissertation and will be published separately as a stand-alone review and meta-analysis article as introduced at the beginning of the section.

Block Copolymers: Self Assembly

Many of the approaches for modeling block copolymer (BCP) phase separation involves the use of self-consistent field theory (SCFT). This involves calculating a local field of interaction potentials that is produced by a test chain and the probability density of these and other energetic interactions. The field produced by the chain is determined which alters the chain energetic terms of neighboring chains whose field in turn affects the test chain in a continuous feedback loop. The goal is to solve for multiple solutions of the total free energy of the system under investigation in order to find the global minimum of the free energy and correlate this with the geometry of the structure that is formed upon the self-assembly as equilibrium is approached. When the chains in a BCP system take on conformations by Gaussian statistics (such is considered in Chapter 1 where the average interaction potentials are constant), there are additional driving forces that restrict the motion of the chains, and these driving forces are different depending on the location of a segment along the chain contour. More simply put, the energy associated with a segment near the junction point will not be the same as a segment near the end of a block. Calculating this free energy primarily relies on two terms that are inversely related: conformational entropy of the chains and interaction energy among unlike monomers. The conformational entropy in SCFT is described in the paragraphs below using the equation for elastic energy of a chain stretching beyond its equilibrium end-to-end distance R . This is calculated from the elastic force of the entropic Gaussian spring $F_{el} = 3k_bTR^2/2nb^2$ which is Eqn 19 from the description of the Rouse model. The mean field model for phase separation reveals particular parameters that are useful when considering the relaxation timescales measured by dielectric measurements in Part I of this dissertation for branched block copolymers. The mean-field approach and these parameters are detailed below for a linear diblock copolymer system.

To begin, an incompressible linear diblock copolymer system having an A and B blocks is shown in Figure 27.

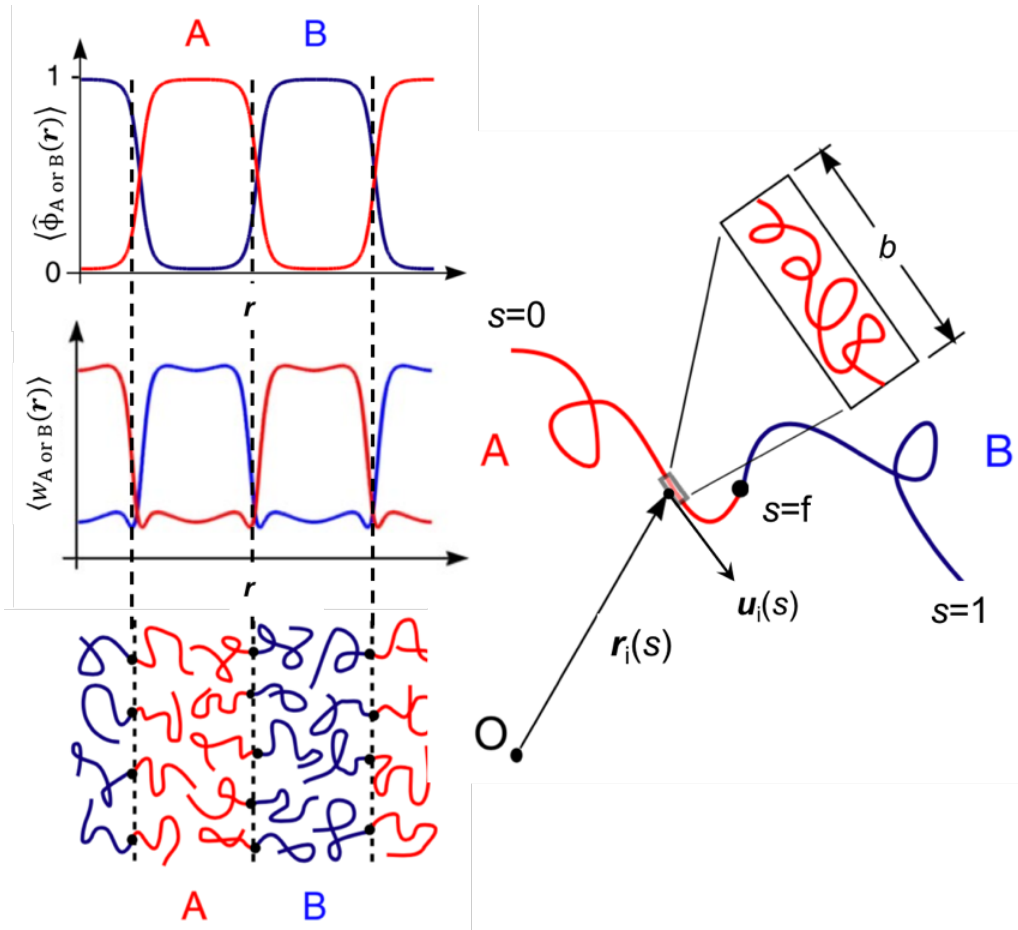


Figure 27: Left is a schematic of an AB block copolymer lamellae (top) with an ensemble average segment density (middle) and fields produced by segments in a block (bottom) as functions of segment position r . On the right, the segment size b and tangent vector $\mathbf{u}$ are specified along with other variables from the main text. Adapted from [101] with permission.

There are n total segments ($n_A + n_B = n$) in a molecule, and the configuration of the i^{th} molecule is defined by a space curve $\mathbf{r}$ as a function of a normalized number of segments s , which is a variable from 0-1 along the chain contour.

The dimensionless segmental concentration $\hat{\phi}_j$ in each block ($j = \text{A block or B block}$) over all locations $\mathbf{r}$ from an arbitrary origin O is calculated by summing over all molecules in the system N for the integral across each block where for $0 < s < f, j = \text{A}$ and $f < s < 1, j = \text{B}$

$$\hat{\phi}_A(\mathbf{r}) = n\rho_0^{-1} \sum_{i=1}^N \int_0^f \delta(\mathbf{r} - \mathbf{r}_A(s)) ds \quad 65a$$

$$\hat{\phi}_B(\mathbf{r}) = n\rho_0^{-1} \sum_{i=1}^N \int_f^1 \delta(\mathbf{r} - \mathbf{r}_B(s)) ds \quad 65b$$

In Eqns. 65a and 65b, ρ_0 is the average segment density over all N and δ is the Dirac delta function. In plain English these equations are articulated as, “at some point s along the chain defined by the position $\mathbf{r}$, the segment density will be equivalent to the average segment density of that block. Since $\hat{\phi}_j$ goes from 0-1 (see Fig. 27) the particular segment at the point along the chain that is representative of the average segment density over all chains is defined to be $\hat{\phi}_j = 1$. If the position $\mathbf{r}$ is not at the segment that is representative of the average segment density among all segments over all chains, then the segment density at that position is defined to be $\hat{\phi}_j = 0$. For $\hat{\phi}_j$ there is no distribution, and the functions are discontinuous (1 at one point, 0 at all others). However, the ensemble average segment density $\langle \hat{\phi}_j \rangle$ is defined for the segments over all molecules that have this average segment at the point $\mathbf{r}$. In other words, $\langle \hat{\phi}_j \rangle$ tells *how far from* the 0-1 is the segment density at that point on the molecule for all molecules. The persistence length $l_p = b\kappa$ for a block is the distance between segments that have completely uncorrelated motions with κ being a parameter for finite bending rigidity (recall for freely jointed chain $\kappa \sim 0.5$). Also, in this interpretation, rather than being the particular Kuhn segment length, b is the segment size for a particular contour length $n/$. Therefore, b can vary depending on the degree of stretching of that

segment with respect to its position s along the chain backbone, and the total chain contour length is nl from Eqn. 3.

As b increases for a segment there is a decrease in available conformations causing the entropy of an individual segment to decrease. In this case, each segment behaves as an entropic spring with an energy of stretching from s_1 to s_2 given by

$$E_s = 3k_b T (2nb^2)^{-1} \int_{s_1}^{s_2} \mathbf{r}_j(s)^2 ds \quad 66$$

which can be deduced from the entropic Gaussian spring from Chapter 1.

When the interaction potentials between unlike segments are accounted for, the total internal energy of the system U can be calculated using the Flory-Huggins parameter for enthalpy of mixing in Eqn. 62 and using Eqns. 65a and 65b to find the equation below which states the internal energy is highest as $s \rightarrow f$ and lowest as $s \rightarrow 1$ or 0.

$$U = k_b T \chi \rho_0 \int \hat{\phi}_A \hat{\phi}_B d\mathbf{r} \quad 67$$

From here, SCFT developed by Helfand borrows from the equation of state in the form of a wave function which was initially used to describe a particle in a potential energy well from quantum mechanics[102, 105, 106]. In other words, rather than a force that directs the system toward equilibrium in classical mechanics, the SCFT uses Hamiltonian mechanics of the wave equation which drives the polymer system toward equilibrium by minimizing its free energy in an external field [107]. The main functions for SCFT are the fields produced by segments of each block by

$$w_A(\mathbf{r}) = \chi n \hat{\phi}_B + \xi \quad 68a$$

$$w_B(\mathbf{r}) = \chi n \hat{\phi}_A + \xi \quad 68b$$

where ξ is a multiplier field accounting for incompressibility by minimizing the segment volume change with pressure across a domain (this is different from the volume associated cooperative segmental motion for the glass transition from Ch. 1). The first terms in Eqns. 68a and 68b represent the attractive or repulsive interactions from Eqn. 62, and $w_{A \text{ or } B}(\mathbf{r})$ are displayed as ensemble averages in Figure 27. The second terms in Eqns. 68a and 68b cause the schematic plot of w in Figure 27 to dip in the middle of a domain. This is due to the segment at this mid-domain point being most representative of a local minimum in the incompressibility term ξ . For an incompressible system, this is negligible, but has been shown to be a factor when experimentally probing a real system.

The total energy of a segment “i” subjected to the interaction field and local stretching (from Eqn 66) is given as a function of $w_j(\mathbf{r})$ below where $j=A$ for $s < f$ and $j=B$ for $s > f$.

$$E_i = k_b T \int_{s_1}^{s_2} 3[2nb^2]^{-1} \mathbf{r}_i(s)^2 + w_j(\mathbf{r}, s) ds \quad 69$$

Thus, from statistical mechanics, the partition function of specific free energy, q (where a partition function is an ensemble of possible states relative to a maximum at $q = 1$), can be calculated as a sum of exponentials for all segment energies up to some particular segment by the following expression

$$q(\mathbf{r}, s) = \sum_{\mathbf{r}_{A \text{ or } B}(0)}^s \exp[-E_i(\mathbf{r}_j, s) (k_b T)^{-1}] \delta(\mathbf{r}_j(s) - \mathbf{r}) \quad 70$$

This equation gives the values for q from 0 or 1 for the segment’s energy as a function of s for a block from 0- s , and $q = 1$ for the highest value of E and accounts for both stretching and interaction potentials.

The free energy partition function of all segments in this field can be expressed as the differential equation

$$\partial/\partial s \, q(\mathbf{r}, s) = (b^2 n/6) \nabla^2 q(\mathbf{r}, s) - w(\mathbf{r}, s) q(\mathbf{r}, s) \quad 71$$

Then, the ensemble average of specific segmental density can then be solved from the partition function [108] of a single polymer molecule for $j = A$ at $0 < s < f$ and $j = B$ at $f < s < 1$, and this is shown below for block A and is represented in Figure 27.

$$\langle \hat{\phi}_A \rangle = V \left[\int_0^1 q_A q_B d\mathbf{r} \right]^{-1} \int_0^f q_A q_B ds \quad 72$$

The above theory is limited to non-bending, planar interfaces (lamellar). The theory states that the total free energy as a sum of chain stretching energies of each block and the energy of surface tension for the interface, and the system reaches equilibrium when G is minimized. For the lamellar interface, the area per junction point $\Sigma = A/N$ for A is the total interfacial area and N is the number of molecules per total volume. The total free energy of the system is then given by

$$G = Nk_b T \left[\left(\pi^2 n / 8 \Sigma^2 \rho_0^2 b^2 \right) + \Sigma \chi^{1/2} 6^{-1/2} \left((\rho_0 b)_A + (\rho_0 b)_B \right) \right] \quad 73$$

where the first term is the interfacial free energy based on the enthalpy of mixing (E_f) and the second terms are estimates the stretching energies E_s of each block. When G is minimized and Σ is held constant, some averaged parameter of curvature $\langle H \rangle$ can be used to model the deviation of G from the ideal non-curved, planar interface. Values of $\langle H \rangle$ are shown as a function of block fraction f in Figure 28 along with possibilities of the free energy for cylindrical domains due to minimizing the distribution of interfacial energy or chain stretching energy to fill the space between domains. A minimization in the distribution of E_s for all chains has been shown to occur for block copolymers with higher Σ and corresponds to higher distribution of E_f across all interfaces, which includes BCPs with branched architectures and linear BCPs with higher PDI for a single block allowing for more complex morphologies.[109]

One of the factors that alters the relaxations of chains in BCP systems compared to homopolymers (summarized in detail in the next section) is the packing frustration of segments within a domain.

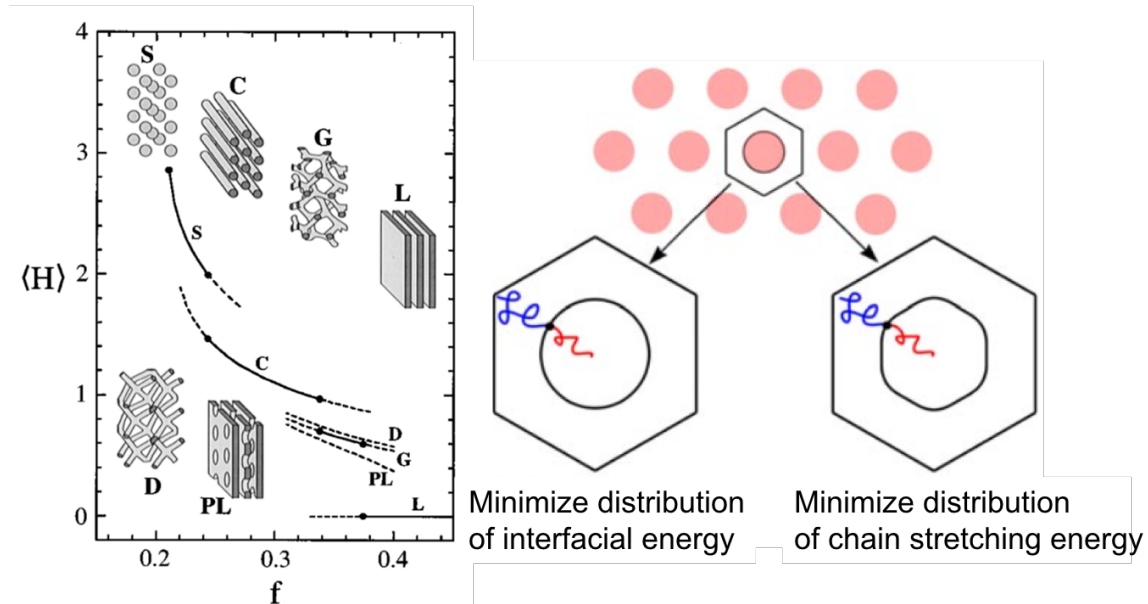


Figure 28: The dependence of interfacial bending parameter H at various block fractions for different morphologies (left). Also, the change in interfacial curvature of a cylindrical domain when distributions of interfacial energy or chain stretching energy are minimized. The trade-off between these two energies during phase separation gives rise to packing frustration Used from [110] (left) and adapted from [102] (right) with permissions.

Packing frustration is a term used for a system attempting to maintain a uniform distribution of E_f across all interfaces by minimizing the total surface area of an interface. This drive is counterbalanced by the requirement to minimize the E_s and thus have uniform chain end-to-end distances $\mathbf{R}$ for all of the chains in a block. For the case of phase-separated BCP systems, $\mathbf{R}$ is greater than for the equilibrated chain described by the Rouse model. Additionally, the Rouse chain is modeled to have isotropic stretching of each segment along the chain contour. The inability for a real BCP system to accommodate both a minimal surface area and uniform stretching causes inhomogeneities in both. Thus, packing frustration can be thought of as an analogy to entanglements for bulk homopolymer systems beyond the Rouse model, but the thermodynamics of BCP phase separation confines chain dynamics well beyond the Reptation model.

Packing frustration is larger for systems with a relative increase in Σ and results in increased heterogeneity in interfacial energy for a block [109]. For example, there is essentially uniform packing frustration in the lamellar morphology, there are homogeneous interfacial energies in the classic cylindrical and spherical morphologies but packing frustration is non-uniform, and the packing frustration is increased for spheres relative to cylinders [111, 112]. The non-classical double-gyroid (D), single-gyroid (G) and perforated-layer (PL) phases shown in Figure 28 have higher degrees of inhomogeneity in interfacial curvature resulting in increased packing frustration among the domains. This inhomogeneity in interfacial curvature may also occur for the C or S morphologies when interfacial energy fluctuations are minimized as shown for a cylindrical unit cell in Figure 28.

For a simple cubic lattice of spherical domains, the distance between neighboring spheres as a function of some location within an interface takes on a geometric distribution as $\langle H \rangle$ changes (depicted in Fig. 29). Since the domains are not uniformly spaced in all directions in the C or S morphologies, the end-to-end distance of the outer matrix chains must also be non-uniform to fill the hexagonal unit cell resulting in a distribution for E_s in Eqn. 66.

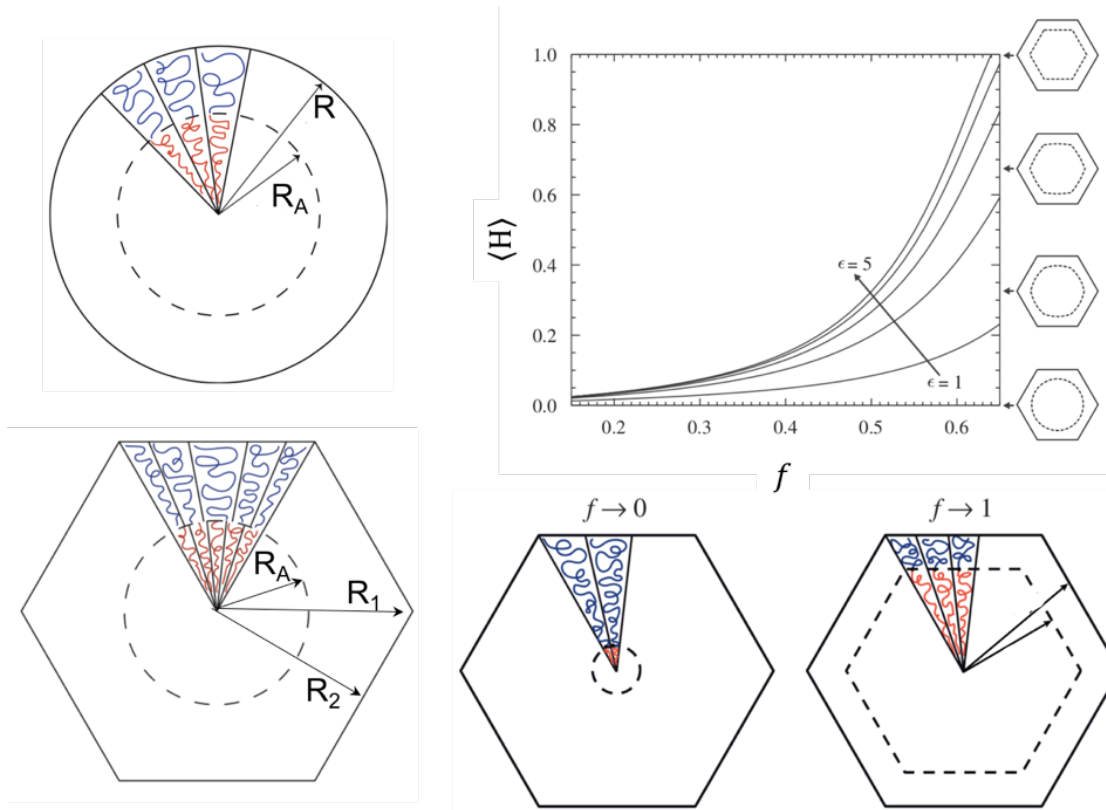


Figure 29: The unit cell of a cylindrical domain for minimizing chain stretching (top left) and maximizing space filling (bottom left). The effect of block fraction on interfacial curvature for different block copolymer asymmetry parameters (top right). This shows interfacial curvature becomes more homogeneous as f and $\epsilon \rightarrow 0$, and chain stretching becomes more homogeneous $f \rightarrow 1$ and ϵ increases (bottom right). Adapted from [109, 113] with permissions.

Therefore, the energy per segment within a single chain from Eqn. 69 will also become disperse across all segments. The unit cell that is produced for phase separation from SCFT for a specific phase geometry is termed the Voronoi, or Wigner-Seitz, cell. The Voronoi cell is useful for considering how $\langle H \rangle$ affects the constituents of E based on location within the domain for some morphology within the context of SCFT. However, the degree of chain end overlap between unit cell has not been considered in the literature, particularly with respect to the conformational entropy and dynamics of the chains.

While SCFT is a powerful tool for rough but accurate estimations of BCP morphology, it is known to return defective metastable minimizations of free energy. Also, additions of an additional block types quickly increases the necessary free parameters that describe the field from two (χ_{AB} and n_A) to five (χ_{AB} , χ_{AC} , χ_{BC} , n_A and n_b)[114]. Furthermore, SCFT is also not a theory to predict relaxation timescales; that is to say it is not a system of harmonic oscillators, but a model for a system of molecules that minimizes energy due to stretching (or entropy) and mixing (or enthalpy). However, it is immensely important for understanding the free energy landscape of a phase separated block copolymer systems particularly for the effect of area per junction Σ . This is particularly useful for comparing the degree of chain stretching across different systems, and for comparing entropic effects of phase separation and may be correlated with the entropy described for the polymer dynamics in the Tube model in Ch. 1.

One way to alleviate packing frustration and create a more uniform interfacial curvature is to incorporate homopolymer chains of a block which will fill the space of more stretched chains. This can allow for a minimizing of the distribution in $\mathbf{R}$ while also minimizing the interfacial energy and results in a more homogeneous Φ and thus sharper ϵ'' relaxation peak shape. This is difficult to mediate in experimental practice because this minimization of both energetic terms by incorporating homopolymer filler will result in measured relaxations of the filler, which then would require a nontrivial deconvolution during analysis.

It may be possible that the forces that are the basis of field theories for phase separation (from chain stretching energy and interfacial energy) can be included as dampening forces to augment the tethered Rouse model to give realistic relaxation dynamics of block copolymer systems. The studies in this dissertation focus on the experimental dynamics of these systems, whose results will be helpful in developing these models. However, since field theoretic simulations are not fully covered here, perhaps they can be developed further in the future to help more accurately describe chain dynamics in block copolymer systems. For now, the awareness of this possibility will be considered when discussing the dynamics measured for the block copolymers in the Chapters to come. A discussion will now conclude this introduction that correlates interfacial energy and chain stretching based on SCFT, and how these parameters may relate to the chain relaxations and dynamics which are just recently being considered in the literature [93].

The chain relaxation on the other hand changes quite a bit compared to PI homopolymer due to non-ergodicity of the chain conformations (not all possible conformational states will be achieved) and will be detailed in the following section for PI at temperatures below the T_g of the PS block which effectively tethers the PI chain to a glassy interface formed during phase separation.

Block Copolymers: Dynamics

This section is separated into

A simple and accurate model that represents the global polarization relaxation of the Type-A chains, specifically poly(*cis*-1,4-isoprene) (PI) in phase separated block copolymer (BCP) systems measured with dielectric experiments, has been the focus of several studies over the past few decades.[73, 89, 93, 115-117] Several reports have aimed to mathematically describe or simulate the constraints on segments and chain motion in phase separated BCP systems to reveal a realistic dielectric chain relaxation (*i.e.* normal mode), but these models

have not been able to reproduce the exact shape of the normal mode process that results from these constraints.[93, 116, 118] The most promising models and experiments have focused on the lamellar microphase separation with some clever investigations on chain dynamics in other microstructures such as cylindrical and spherical domains without identifying specific quantifiable parameters that relate the thermodynamic properties to the dynamics of the chains.[92, 119-126] While the dielectric chain relaxation in block copolymer systems is not typically related directly to applications, it is vitally important in understanding how various physical and thermodynamic constraints alter the dynamic behavior of chains. Fundamental descriptions of the chain dynamics become useful in fine tuning mechanical properties like viscoelasticity of polymeric systems for specific applications.[127-130] The changes in the global relaxation behavior (long time relaxations) which have been analyzed for BCP of differing morphologies by rheology,[131, 132] have not been summarized for dielectric spectroscopy. Generally, the PI chain dynamics in BCPs have been shown to change as other aspects are altered such as morphology, chain orientation, interfacial fluctuation, spatial confinement, thermodynamic constraints, etc.[122, 133-136] However, it remains difficult to apply these various aspects to directly explain the experimentally measured dynamics to a comprehensive model that relates the subtle but informative changes in the dielectric normal mode to the theory. Furthermore, the current methods that are used to quantify these changes are limited to being interesting but incidental anecdotes on the dynamics unless some standard is secured for comparing new studies to those already published.

For the PI homopolymer, there are many studies and reviews that have investigated the dielectric chain relaxation and reveal that the primary dynamical effects beyond Rouse dynamics come about due to entanglement constraints from topological interactions among long chains of increasingly high molecular weights.[48, 50, 52, 57, 58, 61, 64, 65, 69, 74, 133, 137-143] Essentially, multiple normal mode solutions to the Langevin equation of motion for the system of

harmonic oscillators built of N beads connected by springs to form the chain, are measured by applying a small perturbation.[4] The average relaxation $\langle \Phi(t) \rangle$ of all chains back to equilibrium following this perturbation is separated into a linear combination of $p=N-1$ non-stretched exponential modes with τ_p being the relaxation time for that mode.

$$\Phi(t) = g_k \sum_{p=0}^{N-1} \exp(-t/\tau_p) \quad 74$$

The $p=0$ mode is defined as the diffusive center-of-mass solution, and the $p=1$ is the Rouse mode, or the end-to-end vector reorientation mode.[4] Higher order modes are present but their relative intensity g_k is typically negligible under experimental conditions.[50, 63, 64, 66] This system of chains described as beads connected by springs that harmonically oscillate is called the Rouse model.[9] Approaches like the Kremer-Grest model or the Likhtman-Milner-McLiesh model are the most promising representations for applying the Rouse model to entangled homopolymer systems by accounting for entanglements using dynamic tube dilations, constraint release mechanisms, etc.[37, 38] These approaches are based on confinement of the Type-A chains, which have monomeric dipoles within the polymer chain oriented parallel to the chain contour ($\mu_{||}$) that give rise to a polarization response of the normal modes of the chain.[9] The Rouse model has also been applied to chain dynamics of BCPs and accurately describes aspects like the normal mode relaxation time τ_n . [118] However, the topological constraints of entanglement that are described well by the Rouse model have been found to be reduced in phase separated BCPs, and, instead, energetic effects of thermodynamic mixing and entropic chain stretching become the primary factors that alter the dielectric normal modes.

The simulation based studies that show decreased effects of entanglements in phase separated BCPs primarily employ self-consistent field-theory (SCFT).[115, 116, 144] Simply put, SCFT predicts the thermodynamic forces that drive phase-separation which are balanced by the entropic forces that

cause chains to stretch away from the interface which, in turn reduce entanglement interactions.[102] However, this chain stretching energy and inhomogeneous mixing is not embodied in the dynamic responses of the material.[101] Furthermore, SCFT does not provide details for phase separated system of harmonic oscillators on which the Rouse model is based. General effects of chain conformations predicted by SCFT have been used to qualitatively explain changes in the end-to-end dynamics measured for block copolymers, but the theory does not directly consider the normal modes of the chains.[102, 105, 110, 145] Many studies have employed dielectric spectroscopy as an experimental tool, or polarization relaxations as a mathematical tool, to investigate the changes in polymer dynamics based on the effects of various confinements such as phase separation[92, 94, 96, 146], thin films[147, 148], nanoporous media[149-154] and nanoparticle tethered chain or polymer composites[155, 156], but this often requires relatively complicated and subjective data fitting procedures.[157-159]

The few reports that do seek to combine aspects from field theory such as chain stretching energy to explain chain dynamics, address the qualitative changes to the normal mode dielectric relaxation of PI in phase separated BCP. The qualitative change that is observation is primarily described as a *broadened* normal mode that results from various constraints that cause dynamic cooperativity of the neighboring chains. This quality of broadening has been combined with more quantitative functions that describe dielectric data. These functions include the Debye, Cole-Cole, Cole-Davidson and Havriliak-Negami functions, but the shapes of these functions used to describe the chain relaxation in block copolymers have never been standardized as an analytical approach.[87, 160-164] One of the most widely used models to describe the data obtained by dielectric relaxation spectroscopy for PI chain dynamics is the Havriliak-Negami (HN) function (see Eqn. 74). It is derived from the Debye function which describes non-interacting dipole reorientations, but the HN function adds symmetric (α , equal to unity for the Debye function) and asymmetric (γ , equal to unity for the Debye function)

stretching parameters to characterize the reorientation relaxation with a characteristic time τ_{HN} and intensity of the polarization response or dielectric relaxation strength $\Delta\epsilon_{HN}$. [87, 163, 164]

$$\epsilon^*(\omega) - \epsilon_{\infty} = \Delta\epsilon_{HN} / (1 + (i\omega\tau_{HN})^{\alpha})^{\gamma} \quad 75$$

The HN function is an empirical model to describe data as a superposition of many Debye functions with differing weights, but it is reasonably described by the Kohlrausch-Williams-Watts (KWW) function following an inverse Fourier transform to the time domain with added coupling between the high and low frequency behavior of a single relaxation. [165-169] These functions are simply stretched exponentials for relaxation phenomena within the context of fluctuation dissipation theorem. [170] Recent advances have shown that the stretched exponential relaxation described in the frequency domain by the HN function and in the time domain by the KWW function specifically describe motions of overdamped linear oscillators with time-dependent non-Newtonian friction. [171, 172] However, these functions intrinsically do not have a physical basis in polarization relaxation mechanisms beyond those imposed by the Debye model which itself rarely describes orientational diffusion in real systems. The HN and KWW models are used very often as the go-to models to describe polymer relaxations measured by dielectric spectroscopy. A more physical approach to understanding the physics for relaxations with differing spectral shapes of dielectric relaxations uses parameters for the dissipation of energy and the interactions with the medium to find the relaxation function, but this approach is relatively new and has not been rigorously used as a tool to accurately describe these data. [173]

The fitting procedures to the dielectric loss ϵ'' spectra often employ multiple (x) of these HN relaxations (see Eqn. 75) to a single frequency sweep at one temperature. It can be easily seen that letting the 4x parameters free to fit the data can result in an increasingly subjective relaxation shape (see Supporting information for examples). Additionally, the sets of $\epsilon''(\omega)$ data at a single

temperature for PS-PI relaxations based on the meta-analysis of the data in this study have an average of 47 data points. Therefore, as an example, when two HN functions (8 total fitting parameters) and a low frequency conductivity contribution (two fitting parameters, $\epsilon''_{\text{cond.}}(\omega) = \sigma_0/\epsilon_0\omega$) are fit to a data set of 47 points we find a ratio of data points to fitting parameters of 4.7. This, in addition to a lack of physical or statistical representation of the relaxations that these functions describe, results in a high possibility of overfitting the data. For this reason, we finish this review of the PI dielectric normal modes in BCP systems with a meta-analysis of the published PI normal mode relaxation data in the dielectric loss for specific morphologies in linear diblock copolymers with PS and PDMS counter blocks. We have organized the data from three categories of PI chain relaxation in BCPs: 1) well-ordered phases below the T_g of the counter block; 2) well-ordered phases with a rubbery counter block; and 3) disordered or poorly ordered phases. In this way the shape of the relaxation can be directed by statistical power rather than arbitrarily and unscientifically changing shape parameters to represent the data.

Using the HN function to Analyze PI Dielectric Relaxations

The HN function for the measured PI chain relaxations is typically fit in the dielectric loss ϵ'' representation of the dielectric data to match the shape of obvious and/or hidden relaxation peaks by[49]

$$\epsilon''_{\text{HN}}(\omega) = [\Delta\epsilon_{\text{HN}} \sin(\gamma\psi_2)] [1+\psi_1^2+2\psi_1\sin((1-\alpha)\pi/2)]^{-\gamma/2} \quad 76$$

$$\text{where} \quad \psi_1 = (\omega T_{\text{HN}})^\alpha$$

$$\text{and} \quad \psi_2 = [\arctan(\psi_1 \cos((1-\alpha)\pi/2))] [1+\psi_1\sin((1-\alpha)\pi/2)]^{-1}$$

Generally, the intensity or dielectric relaxation strength of the normal mode $\Delta\epsilon_n$ (see Eqn. 77a) is modeled by the length of the end-to-end dipole vector $\langle r^2 \rangle$

and the number density or concentration ϕ of those dipoles, and is quantified in the HN function by integrating the fit to the relaxation in the ϵ'' data through Eqn. 77b.

$$\Delta\epsilon_n = 4\pi N_a \mu_{||}^2 F g \phi \langle r^2 \rangle (3k_B T M)^{-1} \quad 77a$$

$$\Delta\epsilon_{HN} = 2\pi^{-1} \int_0^\infty \epsilon''(\omega) d \ln \omega \quad 77b$$

In Eqn 77a, T is the absolute temperature, k_B is the Boltzmann constant, N_a is Avogadro's number, and M is the molecular weight of the Type-A chain. Eqn. 77a shows that the $\Delta\epsilon_n$ follows an inverse temperature T dependence based on the theory for the Type-A polymer.[49] For PI normal mode in PS-PI BCP the $\Delta\epsilon_n$ value is often used as evidence of changes in the chain end-to-end distance relative to another similar PS-PI polymer. This can be tricky due to possible morphology changes and contributions from the g term in Eqn. 77a that can follow these changes based on chain conformation. Studies indicate that $\Delta\epsilon_n$ increases as morphologies change for a constant PI block molecular weight from PI spheres, PI cylinders, lamellae, PS cylinders/spheres. [120, 125, 133, 174] This indication has not been shown directly by a single study but is intuitive based on the dielectric theory of the Type-A polymer and from chain conformational changes with varied morphology suggested by SCFT.[102, 108, 110, 175, 176]

Finally, cross-correlations of the orientational polarizations of the chain end to end dipole are often represented using the Kirkwood correlation factor g in Eqn. 77a which accounts for heterogeneous chain dipole orientations. Based on mathematical studies published over half a century ago, $g = 1 + \sum_{ij} \cos \theta_{ij}$ where θ is the angle between the end-to-end vector of the i^{th} test chain and the j^{th} nearest neighbor chains.[177-179] The value $g = 1$ occurs for truly random average dipole orientations.[180] Relative changes in $\Delta\epsilon_n$ have been explained using possible orientational cross-correlations of PI chains in block copolymers through the dielectric response function. Direct evidence of these cross-correlations is limited in the studies that make such claims using dielectric spectroscopy to study the PI

chain dynamics.[56, 95, 124, 125, 181] Other techniques such as NMR, FRS and neutron scattering have provided more direct evidence of this chain correlation in similar materials, but often this claim of a change in g is mentioned as a possible reason for changes in $\Delta\epsilon_n$ not necessarily by direct evidence.[27, 45, 182-184]

The α -relaxation of PI which reflects the relaxation of the dipole moment within but perpendicular to the polymer backbone ($\mu_{\perp}$) is measured at lower temperatures approaching the T_g at which the characteristic rate of the α -relaxation $\tau_{\alpha} \sim 100$ s. The temperature dependent rates of the PI α relaxation in well-ordered BCP phases is nearly identical, if not slightly slower compared to the same process in the homopolymer. From the data that are included in this study for BCP above the order disorder transition (ODT), the HN shape of the PI α -relaxation in linear diblock copolymers when fit to the data in combination with the PI normal mode is $\alpha = 0.59 \pm 0.05$ and $\gamma = 0.5 \pm 0.2$. [92, 119, 120, 174, 185, 186] The relaxation strength $\Delta\epsilon_{\alpha}$ of this process is related to the concentration of segments and the friction coefficient for the diffusion of these segments through

$$\Delta\epsilon_{\alpha} = \mu_{\perp}^2 N (3\epsilon_0 k_B T V)^{-1} \quad 78$$

where T is the absolute temperature, k_B is the Boltzmann constant, N is the number of dipoles contributing to the relaxation in a volume V and ϵ_0 is the vacuum permittivity. The ratio of the dielectric strength of the PI normal mode to the dielectric strength of the PI α -relaxation has never been a consistently reported value in dielectric studies of PS-PI systems. For the homopolymer where an average orientation of the chains is truly random, $\Delta\epsilon_n \Delta\epsilon_{\alpha}^{-1}$ gives the number of segments contributing to chain dipole reorientations relative to segmental dipoles. For the entangled homopolymer PI, this ratio is relatively constant at ~ 1.25 and closer to unity for lower molecular weights.[46, 61] The dipole moments perpendicular and parallel to the backbone, while contributing separately to the dielectric response, are very much correlated. For homopolymer systems, the Mode Coupling Theory reveals that correlations of segmental friction and the

motion of the entire chain are not discrete, and normal modes of the chains become coupled when entanglement are introduced.[20, 77, 80] As such, the ratio of the normal mode and the segmental relaxation strengths ($\Delta\epsilon_n$ and $\Delta\epsilon_\alpha$, respectively) can then give important information regarding the relative contributions from these relaxations to the dielectric spectrum.

The HN parameters for the chain relaxation of monodisperse, linear PI systems are $\alpha = 1$ and $\gamma = 0.45 \pm 0.05$, where the increase in γ from 0.4 to 0.5 results in asymmetric broadening of the chain relaxation toward high frequencies described by the various theories.[37, 46, 68] This high frequency broadening is due to contributions of higher order (faster) eigenmodes to the dielectric spectrum for chains with $M > M_c$ due to entanglements (see g_k in Eqn. 74). Toward low frequencies, the slope of the ϵ'' peak for the normal mode of PI homopolymer scales with ω^{-1} corresponding to terminal relaxation or complete reorientation of the end-to-end dipole vector.[48, 57, 61, 65] This terminal behavior is rarely observed for the PI normal mode in phase separated BCPs, especially when the counter block is glassy. Finally, based on the enthalpic and entropic penalties of phase separation, it has been suggested that diffusion of the junction point within the interface in the strong segregation regime that results in center of mass diffusion only occurs in 1D for cylindrical morphology, 2D in lamellae and 3D for gyroidal.[187] This center of mass diffusion does not imply terminal relaxation behavior, but does cause anisotropy in the relaxations measured by dielectric experiments.

Block copolymer diffusion perpendicular to the interface must overcome an enthalpic energy barrier, and diffusion parallel to the interface must overcome an entropic energy barrier termed “activated reptation” and “block retraction”, respectively.[187, 188] This diffusion is not necessarily the same as the polarization relaxation measured by DS. However, the polarization response of the dielectric normal mode may be activated by these block copolymer diffusion mechanisms. Another similar mechanism, termed “hopping” diffusion, was

described as diffusion of a junction point from one discrete domain to another in a similar way to activated reptation.[189] When the block copolymers thermodynamics favor phase separate, this activated hopping diffusion is possible, and thus causes the diffusion coefficients to be multimodal. The normal modes or end-to-end chain or sub-chain dipole fluctuations in these relative directions have been separated in simulations for characterizing the dielectric chain relaxation in phase separated systems. These studies show that when a chain is tethered to a solid interface (no thermodynamics) the predicted relaxation times for parallel modes are slower than the perpendicular ones, but when the entropy of mixing (χN) is included for phase separation, the parallel modes are slowed even more due to chains entropically stretching away from the interface to offset the enthalpic penalty.[93, 116, 123, 147] Similarly, several authors have modeled the correlation function of the mean squared displacement and end-to-end vectors perpendicular and parallel to the interface. These studies found that for well separated domains, the long timescale motions that occur perpendicular to the interface reach a plateau while the long timescale motions parallel to the interface continue to relax, and the parallel and perpendicular modes are ultimately decoupled at long times.[120, 121, 190] This is in accordance with the studies that report BCP diffusion occurring near or below the ODT in which the thermodynamic penalty of mixing is overcome (enthalpic barrier is small) one block is able to “retract” or pass through the non-like neighboring domain.[115, 191] When the interface is fully defined and this entropic barrier is large such that it is not overcome at experimental timescales and temperatures, true self-diffusion (or polymer center of mass motion) is only measured when the junction point diffuses within the interface.[187, 192]

The quantitative nature of describing changes to the shape of the dielectric normal mode relaxation and the increasingly large number of published data for PI in phase separated systems may be a good way to create a standard in the response measured by polarization relaxations of Type-A PI chains. In the meta-

analysis of this mini-review, we have organized the PI dielectric normal mode data published for lamellae forming poly(styrene-*b-cis*-1,4-isoprene) (PS-PI) BCP, with additional perspectives from other morphologies and BCP chemistries (*i.e.* PDMS-PI, PS-PI/PI blends, etc.) in an attempt to provide a standard description of the shape of the PI chain relaxation in phase separated systems based on the HN fitting parameters. This is then used to identify the physical aspects of the chain confinements that may be refined in future experimental and mathematical studies that aim to understand how effects beyond phase separation such as nanoparticle composites, charge transport or topological chain architecture modify or take advantage of these chain dynamics.

PI Dielectric Normal Mode with Glassy Counter Block

When the PI block exists in a well-ordered system and the counter block is in the glassy state, such as with PS, the dynamics of the PI block can be considered as a tethered chain to an immobile interface. In such a case, there is effectively no diffusion and limited motion of the PI chains perpendicular to that interface. In this section, we exclusively examine the PI normal modes in PS-PI BCPs where well-defined morphologies are formed, and where measurements are taken at $T < T_g$ of the PS block such that only the PI dynamics are measured. Additionally, the shapes of the normal modes are considered for different morphologies and the differing constraints on the PI chains therein are discussed.

Lamellae Morphology

A majority of the dielectric investigations into the PI chain relaxations in PS-PI at $T < T_g$ of the PS block are for systems that form lamellar morphologies. These data are summarized in Figure 30 with our HN fits to the PI normal modes and the PI α -relaxation if necessary.

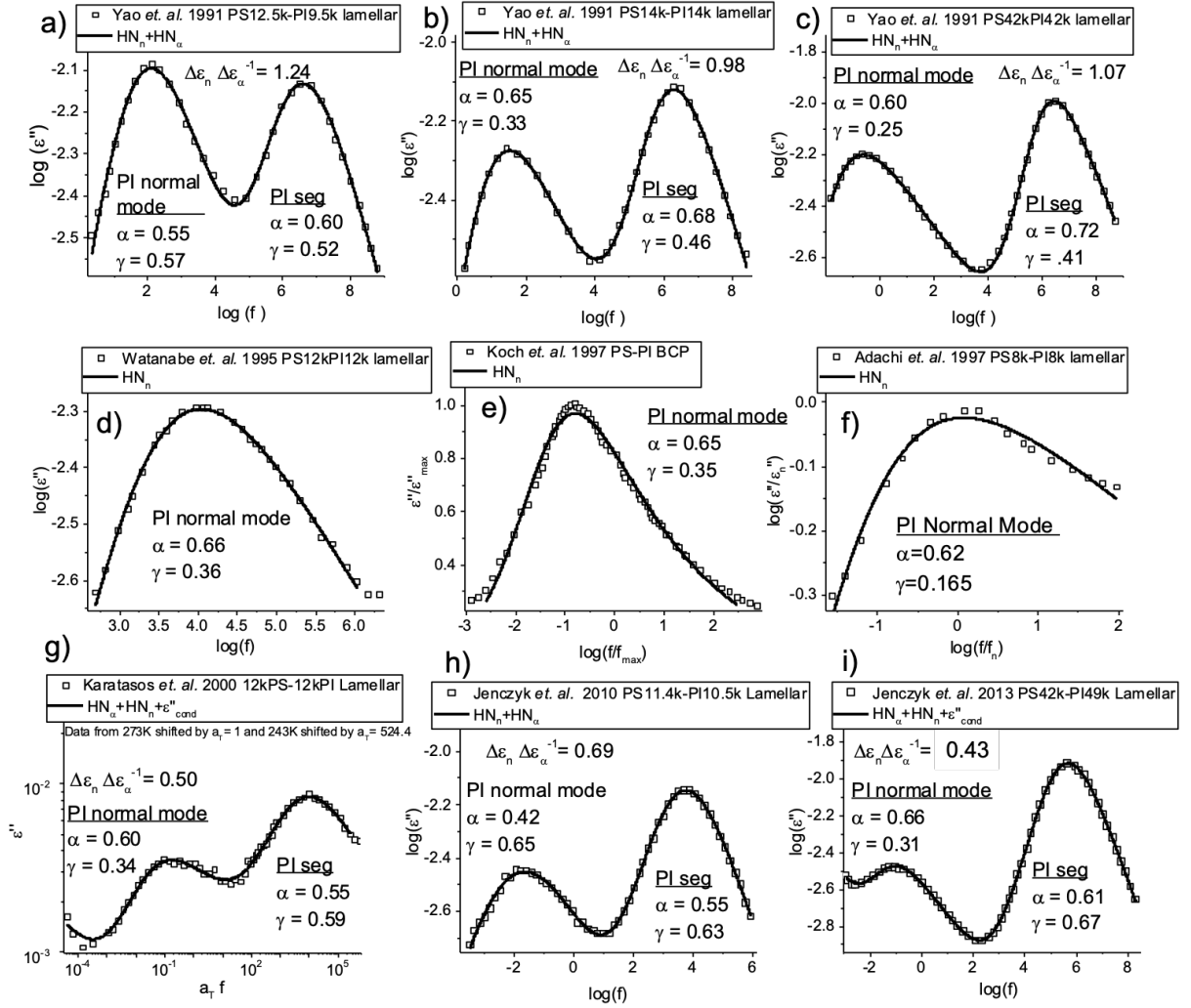


Figure 30: Reproduced frequency dependent dielectric relaxation spectra of PI in PS-PI systems at $T < T_g$ of the PS block from the literature. Each plot was fit with representative HN functions for the PI chain relaxation (“PI normal mode”) and/or the segmental motions of the PI α -relaxation (“PI seg”) and a low frequency conductivity contribution if necessary. Data for (a-c) is from [92], data for (d) is published in both [56, 126], data for (e) is from [116], data for (f) is from [133], data for (g) is from [95], data for (h) is from [185] and data for (i) is from [119]. All data is reproduced with permissions, except for the data in (f).

The foundational studies were by Yao *et. al.* who reported that the PI chain relaxation in block copolymer systems shows that the polarization is representative of isolated chains and that polarization of neighboring chain dipoles do not cross correlate. These authors postulated that the cooperative motions within a domain cause the dynamical changes that are observed in the dielectric normal mode [92].

Another series of studies by Watanabe and coworkers starting in 1995 compared the dynamics of PS-PI BCP as a representation for dangling PI chain ends (see Fig. 30d) to the PI normal modes of a PS-PI-PS triblock system with dipole inversion of the PI midblock to reveal the role of loops and bridges.[56, 124, 126, 136] Their major finding, apart from estimating the fraction of loops and bridges, is that there is an increase in the $\Delta\epsilon_n$ due to knotted chains whose motion is coupled causing cross terms in g to be non-zero.[56] These knots are much less likely to occur for the linear diblock system due to reduced effects of entanglement that are driven by thermodynamic phase separation. An interesting note that we have considered in the current review and meta-analysis is that it appears the same data for the 12kPS-12kPI diblock originally from the 1995 study has been reproduced in two other publication; thus we have only incorporated it once for the statistical analysis of the chain relaxation shape.[56, 95, 126] Furthermore, a recent publication details the results of gradient PS-PI copolymers with an increasingly tapered composition of the middle portion of the block copolymer causing a broadened interphase. The dielectric relaxation of the PI sub-chain end-group was reported to have a reduced relaxation strength relative to that of the PI segmental process as the molecular weight of the gradient portion was increased.[135]

The data in Figure 30e is of a non-descript PS-PI block copolymer measured by Dr. B Stühn for a study that mathematically described the dielectric normal modes of a tethered Rouse chain to an interface showing that the measured full width at half max is increased for the lamellar system compared to the homopolymer.[116] Their results suggested that the broadened PI normal

modes in the phase separated system is due to decoupled relaxations in directions perpendicular and parallel to the interfacial plane which has been explored in other mathematical and experimental studies as well. [93, 193, 194] A similar argument from the Adachi *et. al.* paper (see Fig. 30f) shows that the PI chain relaxation peak broadens in three PS-PI systems as the morphology changes.[133] The Karatasos *et. al.* data in Figure 30g are of a phase separated system from a study of PS-PI systems near the ODT.[95]

Lastly, two publications by Jenczyk and coworkers compared dielectric data of lamellae forming PS-PI with NMR spin lattice experiments. They report the HN parameters of the normal mode and α relaxation which are different from our fits, which is likely due to the use of the same Cole-Cole α -relaxation shape for the PI block as the PI homopolymer ($\alpha \sim 0.6$, $\gamma=1$). Table 3 shows our α -relaxation fit parameters for the data in Figure 30a-c, 30g-l which are fit with a linear combination of HN fits for the α and normal mode relaxations. We show that fitting the PI α relaxation in combination with the normal mode results in symmetric and asymmetric stretching parameters that average to $\alpha= 0.62$ and $\gamma=0.55$ for the former process. When the PI α relaxation is fit separately from the normal mode, the shape is described by the Cole-Cole function. This Cole-Cole shape, however, is inaccurate due to the overlap of the two relaxations. Additionally, the ratios of the relaxation strengths of the normal mode to the α -relaxation are shown in Figure 30 for systems that include the faster relaxation. These values are relatively low compared to the homopolymer and may be due to canceled dipole vectors on opposite lamellar planes. This will be discussed further when the “slow” mode is analyzed. In Figure 31, all of the normal mode data from Figure 30 with the HN fit to the α relaxation and conductivity contributions subtracted are normalized by the volume fraction of PI in the BCP and by the frequency (f_n) of maximum loss of the normal mode. Figure 31 also shows the weighted averaged HN shape parameters from the 10 polymers in Figure 30, revealing that the relaxation peak of a PI block in well-defined lamellae with a glassy PS block has a constant shape.

Table 3: PI α -relaxation HN parameters for PS-PI systems at $T < T_g$ of PS from the literature

Paper, PS-PI polymer	α	γ
Yao 1991, 41.5k-42.5k	0.72	0.41
Yao 1991, 14.1k-14.9k	0.68	0.46
Yao 1991, 12.5k-9.5k	0.6	0.52
Jenczyk 2013, 41.8k-49.1k	0.61	0.67
Jenczyk 2010, 11.4k-10.5k	0.55	0.63
Karatasos 2000, 12k-12k	0.55	0.6

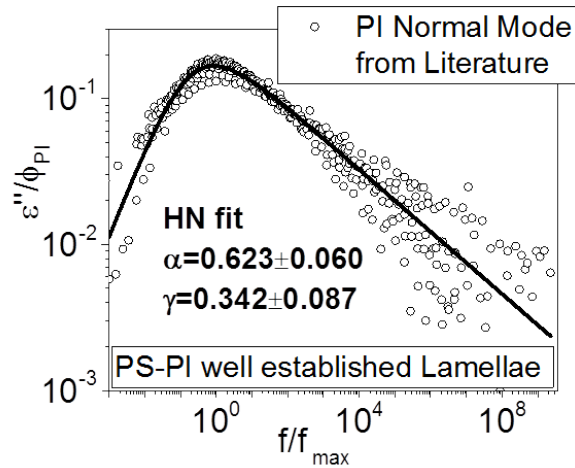


Figure 31: The dielectric loss data (normalized by PI volume fraction in the BCP and the frequency of maximum loss) of the PI normal modes from Fig. 30 with the HN α -relaxation and $\epsilon''_{cond.}$ fits subtracted. The solid line shows the HN fit with the averaged shape parameters based on statistical analysis in the Supporting Information.

Non-Lamellae Morphology

Reports of PS-PI forming PS spherical domains show that the dynamics of the PI chains resemble that of PI stars with arm retraction relaxations and terminal relaxation is only achieved when the PS micelles diffuse by the Stokes-Einstein mechanism.[4, 195-197] The relaxation of PI chains in homopolymer stars have also been extensively studied and modeled.[51-53, 63, 138, 143, 196, 198-203] These dynamics are similar to linear PI with dipole inversion, and are very sensitive to dispersity of arm lengths.[51, 195, 203]

There are very few studies that directly measure PI dielectric chain relaxation in PS-PI systems that form PS cylinders or PI cylinders.[126, 158, 182] Therefore, we measured two polymers that fall on the PS-PI phase diagram for these two morphologies (16.5kPS-30.5kPI and 72kPS-13kPI) [100, 204] for comparison to the limited data from the literature. The shapes of the normal modes of our polymers do in fact match those from the literature (see Figs. 32 and 33). The HN parameters for the PI in cylinders was found to be $\alpha=0.38$ and $\gamma=0.52$ (see Fig. 32) [126, 182]. For the PS in cylinders the PI normal mode was found to have HN parameters of $\alpha=0.43$ and $\gamma=0.75$ (see Fig. 33) [158]. Very little can be gathered from this other than the fact that motion parallel to the interface is essentially 1D for PI in cylinders, and gives rise to the most broad normal mode HN shape. The normal modes of PI in cylinders with a rubbery counter block has the same HN shape that as those in Figure 30. The broadened HN shapes in Figure 32 are likely due to the inability for the 1D diffusion of the PI in the cylinders because of the glassy PS block, whereas with PDMS diffusion of the junction point within the interface is possible as discussed later.

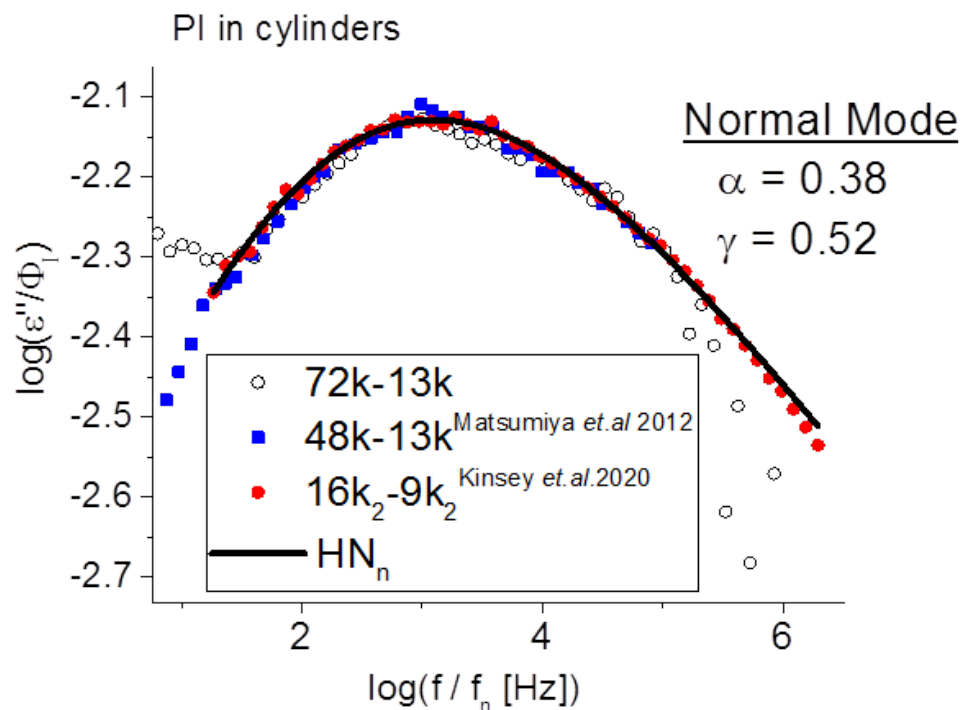


Figure 32: The dielectric loss of the PI normal mode in PS-PI systems that form cylindrical PI phases. Data in blue is from [126] and data in red is from Chapter 6 [182], and both are used with permission. The HN fit to this data is shown as a black line. We note that the data in red circles are of a PS₂-PI₂ miktoarm star copolymer with PI cylinder morphology from a publication showing that the symmetric architecture results in the same normal mode relaxation shape as the linear diblock system.

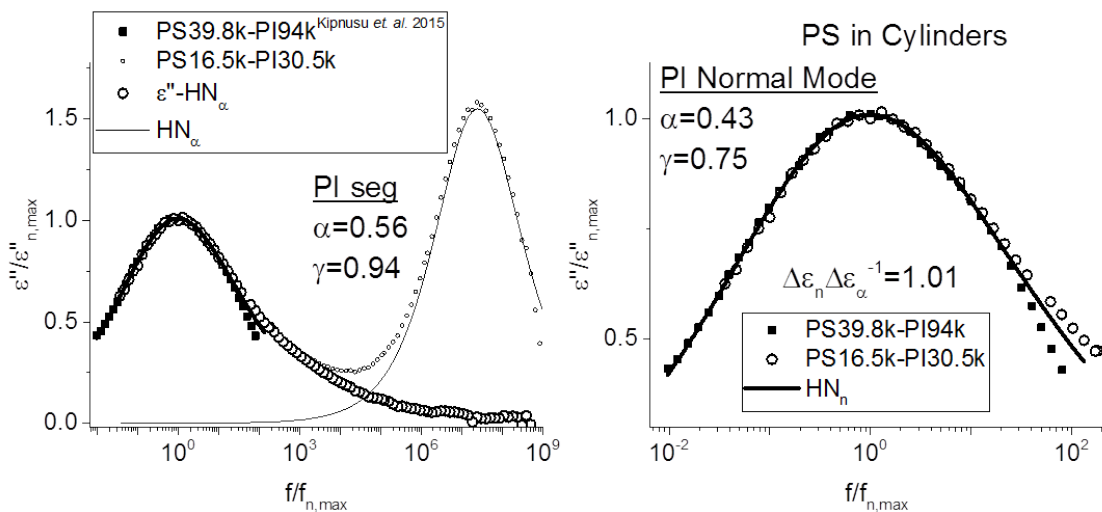


Figure 33:The dielectric loss of the PI normal mode in PS-PI systems that form cylindrical PS phases. The data in solid symbols are used from [158] with permission. The left panel shows the full spectrum of our polymer with the PI α -relaxation fit and the subtracted data. The right panel compares the PI normal modes and shows the HN fit.

Finally, to our knowledge PI in spheres for PS-PI systems has only been reported once, and a nearly flat loss curve was measured for the PI normal mode.[126] The geometry of the morphology allows almost no motion parallel to the interface, which intuitively would result in very few chains contributing to the relaxation. However, we believe that the PI chain relaxation can be measured for discrete sphere-like PI in imperfect spheres which are found in Frank Kasper σ phases and are modeled by the Voronoi cell.[108, 205, 206]

The effect of the spatial confinement of PI in discrete PI phases (restriction of degrees of freedom due to geometric space) was investigated by blending PI homopolymer with PS-PI and PS-PI-PS block copolymers.[125, 207] The resulting homopolymer PI normal mode shape when blended with the BCP nearly matched that of the bulk homopolymer, and had a peak at slightly higher frequency. This confirmed that the thermodynamics driving phase separation modifies the measured response of the homopolymer chains, and these modifications are increased from lamellae, PI in cylinders to PI in spheres. As such, an expansion of SCFT that considers the normal modes of harmonic oscillators would be very useful.

Normal Mode with Rubbery Counter Block or Near the OTD: The Slow Mode

Several reports have indicated a slow “interfacial” relaxation measured by BDS at temperatures above the T_g of the counter block in PS-PI and PI-PDMS systems and for PI blocks in systems near the ODT.[94, 96, 185] It must be noted that this slow mode occurs at similar temperatures, timescales and loss intensities as the PS α -relaxation. The two must be carefully parsed, otherwise improper diagnosis of the PS α -relaxation as the slow mode might occur which may be the case in some studies, especially above $\sim 360\text{K}$ (close to the ODT and/or the PS T_g) where strong ionic conductivity contributions typically dominate the loss spectra making it difficult to analyze any dipolar relaxation.[92, 94, 95] Additionally, the

fitting of multiple overlapping and hidden relaxations with the HN functions can be easily overfit as discussed earlier. Nonetheless, the normal mode and slow mode measured for several systems are discussed in this section for lamellar systems, and for PI in cylinders for PI-PDMS systems.

A study by Karatasos *et. al.* observed a relaxation slower than the PI normal mode in PS-PI polymers at $T < T_g$ of the PS block near the ODT due to a low BCP molecular weight, and they used a CONTIN procedure to calculate the relaxation time distribution function from the dielectric data and did not use any HN fits.[94] We reanalyzed the data of the ordered 8.2k-8.2k and 6.1k-6.1k polymers (low χ_N) from this study with HN fits (see Fig. 34), of which the normal mode is included in our statistical analysis. The slow mode for both polymers was slower than the normal mode by a factor of ~ 500 and had CC α fitting parameters of 0.68 and 0.58, respectively.[94] These CC α parameters are similar to the slow mode parameters for the PI-PDMS polymers which have possible hopping diffusion or activated reptation mechanisms. Data for the PI α -relaxation was not reported, and therefore, the ratio of the dielectric strengths of the PI segmental and chain relaxations could not be determined. However, they did report that, in comparison to the melt pressed sample preparation, the loss intensity of the slow mode for the 8.2k-8.2k increased by a factor of three following slow solvent casting which tends to result in longer range order for phase separation. If the slow mode is indeed a normal mode perpendicular to the interface, then an increase in long range order with lamellae oriented perpendicular to the electrodes would result in this increase. Additionally, with these specific polymers having molecular weights just near the ODT, the small PI block size may have resulted in a fast enough perpendicular normal mode that it could be measured at frequencies higher than the PS α relaxation.

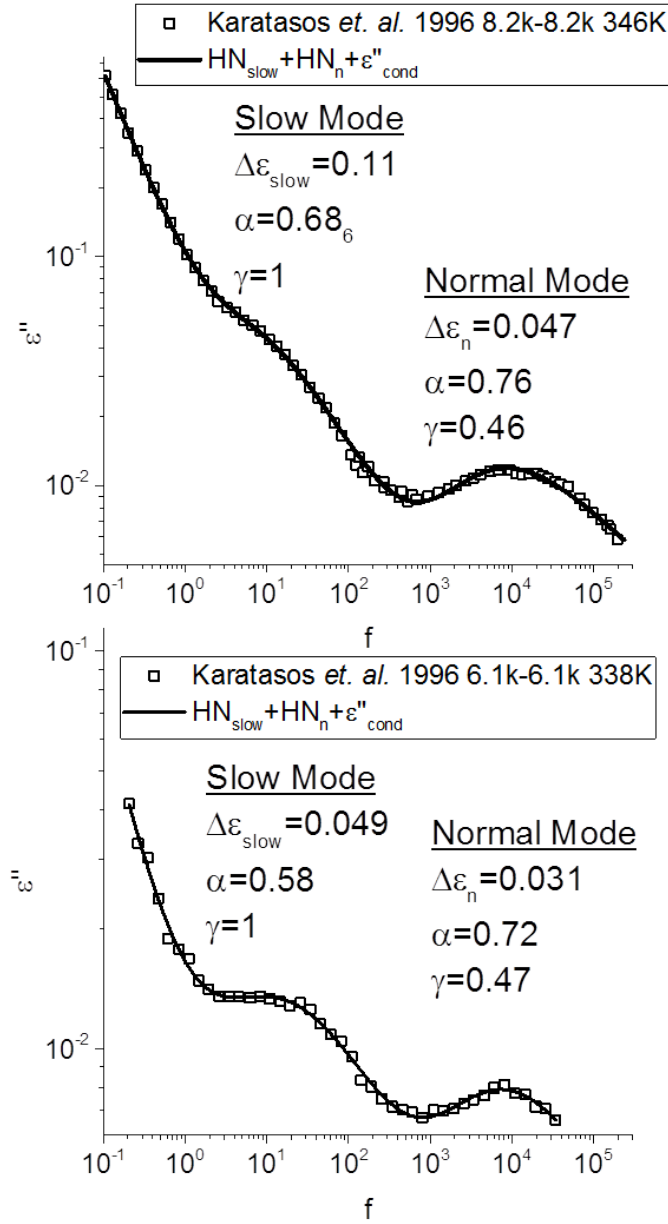


Figure 34: Dielectric loss of the PI normal mode and slow mode for low molecular weight PS-PI systems near the ODT. These data are used from [94] with permission. The shape parameters of these relaxations are shown in the plots. The normal mode shape parameters are noticeably similar to those in Table 3.

To further this argument of separated PI normal modes perpendicular and parallel to the lamellar interface, we discuss the experiments by Meins *et. al.* (data not shown) who experimentally show that this slow relaxation is only measured when the PS-PI interface is no longer glassy and that the slow relaxation is altered when the orientation of the domain interface changes with respect to the electrodes.[194] At $T > T_g$ of the PS block the enthalpic barrier to true BCP diffusion is overcome allowing the PI block to diffuse through activated reptation. Following alignment of the lamellar planes parallel to the electrodes (*i.e.* the anisotropic chain modes probed were perpendicular to the interface), the $\Delta\epsilon_n$ decreased suggesting a reduced number density of dipoles contributing to that relaxation. This study published the HN shape parameters for the normal mode and “slow” mode relaxation for the materials with randomly oriented lamellae which are included in the meta-analysis, but they did not publish the specific shape parameters in the oriented lamella systems. They did however report the $\Delta\epsilon$ for each mode following orientation, and the faster parallel normal mode was not observable following orientation perpendicular to the electrodes.

In another paper, the $\Delta\epsilon_n$ of the PI in PS-PI near the ODT was reported to decrease from 0.11 at 280 K to 0.07 at 373K with the PI $\Delta\epsilon_\alpha = 0.06$ giving a $\Delta\epsilon_n \Delta\epsilon_\alpha^{-1}$ ratio of 1.83 - 1.17.[208] Compared to the relatively low ratios displayed in Figure 30, these increased values of $\Delta\epsilon_n \Delta\epsilon_\alpha^{-1}$ at low temperature may be due to either an increase in $\langle r^2 \rangle$ from Eqn. 77a in disordered system or decrease in $\Delta\epsilon_\alpha$ due to changes in monomeric friction. Either possibility reveal that the likely random orientation of PI chains in the disordered state results in the ratios of the dielectric strengths to be similar to that observed for the homopolymer which is assumed to have completely random orientations. For the reduced $\Delta\epsilon_n \Delta\epsilon_\alpha^{-1}$ in Figure 30, one might expect the dielectrically active normal modes perpendicular to the plane of the interface of chains on opposing sides of the lamellae to be reduced in the dielectric signal due to canceled vectors. We cannot rule this out due to non-oriented lamellae, and additional studies will be necessary to identify

contributions from cross-correlated chain dipoles. Additionally, the signal may be canceled or reduced in intensity until the interface became mobile enough, as for the systems in this section to measure a polarization relaxation that otherwise would be constrained by an immobile surface.

In Figures 35 and 36, normal mode data for PI-PDMS systems are shown and in instances where the activation reptation energy barrier is low (*i.e.* low PDMS block molecular weight producing the lamellae phases) the slow mode is observed at lower frequencies.[120, 174, 186] Again, this slow mode, which is only observed for the low PDMS block molecular weight samples, is discussed in terms of undulations of the interface. However, with a rubbery PDMS block, these undulations may be expected for the non-lamellar forming systems in Figure 36 in which a slow mode is not observed. Either way, this type of interfacial undulation motion ultimately results in motion of the PI chain perpendicular to the interface. From all of the systems where the PI slow mode is observed, the relative energy barrier for activated reptation is expectedly low, and therefore full BCP diffusion is possible. In such a case, the slower center of mass diffusion mode $p=0$ can be dielectrically active. Furthermore, the similarity in the PI normal mode HN shapes across all samples where PI motion parallel to the interface is possible suggests that the motion for this relaxation is comparable regardless of the system under investigation. For the non-lamellar systems with PS, PI motion parallel to the interface is reduced because of morphological restrictions in conjunction with the glassy PS interface, while for the lamellae samples with PS, only the glassy interface restricts motion (*e.g.* 2D degrees of freedom for lamellae compared to 1D in cylinders where motion is restricted when the counter block is glassy). When the glassy interface restriction is lifted in the cases of a PDMS counter block (see data in Fig. 36) the normal mode relaxation shapes match those observed for the lamellae systems.

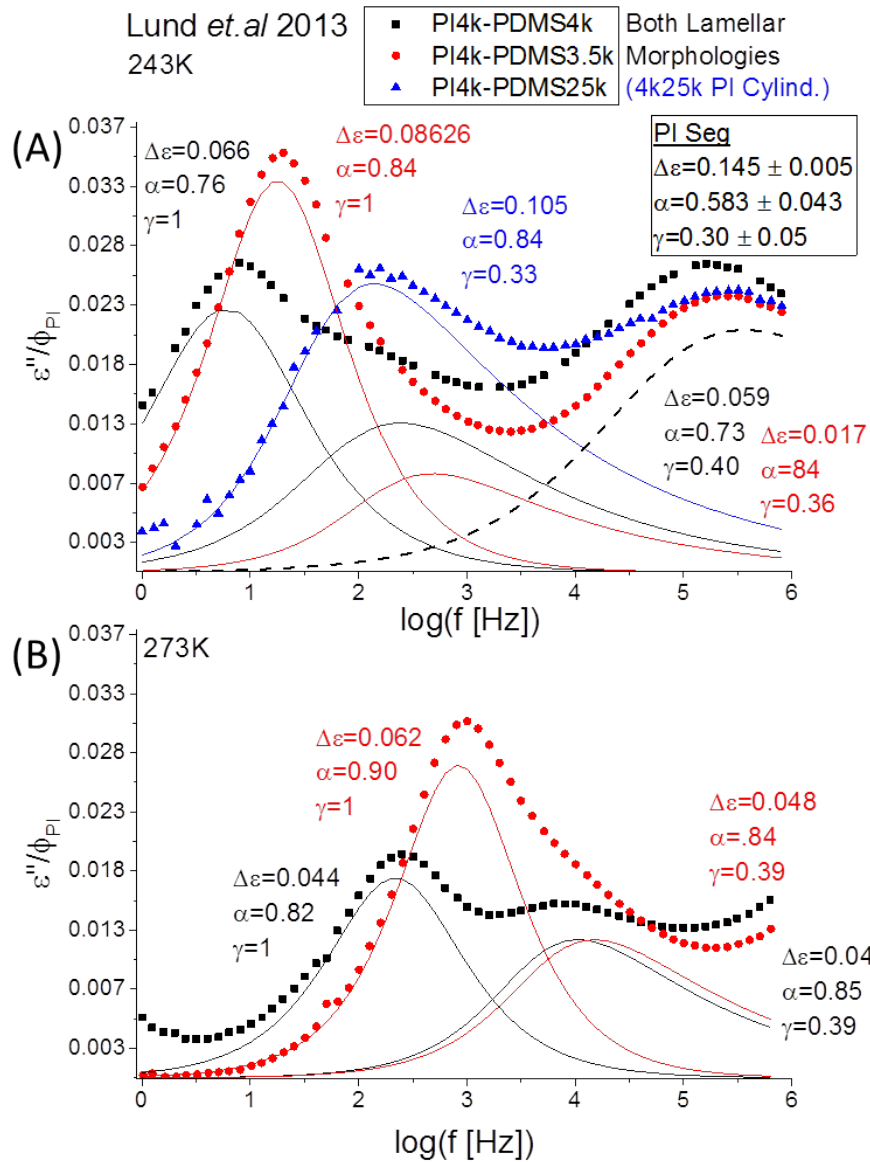


Figure 35: The low temperature dielectric loss spectra of two lamellar PI-PDMS polymers where a the α -relaxation, normal mode, and slow mode are observed (top panel, black and red data) and for cylindrical PI phase with similar PI molecular weight where no slow mode is observed (top panel, blue data). These data are from [120] and used with permission. The bottom panel shows the data for the lamellae systems at a slightly higher temperature. The slow mode is modeled by the Cole Cole function and the normal mode and α -relaxation HN parameters in all cases are similar to those for the data in Fig. 30.

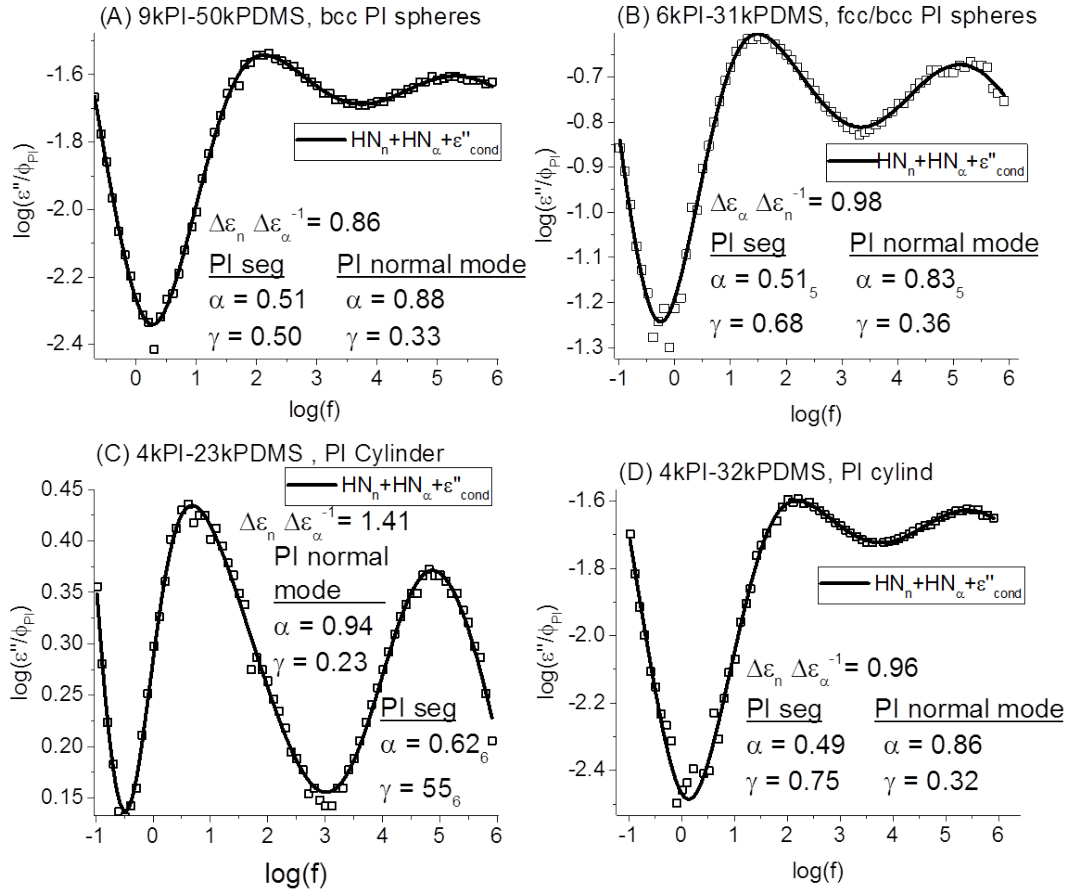


Figure 36: Dielectric loss data at single temperatures for PI α -relaxation and normal mode for PI-PDMS systems forming continuous PMDS phases and discrete (spheres or cylinders) PI phases. The data in (a-c) are from [186] and for (d) is from [174], and are used with permission. There is no slow relaxation observed in any of these spectra, which is likely due to a large energetic barrier for PI diffusion perpendicular to the interface that results from a large PDMS block. The HN shape parameters are noted in each figure which are similar to those for the data in Fig. 30.

Thus, based on the meta-analysis of all of the dielectric normal modes of PI in PS-PI systems and PI-PDMS systems from the literature, we strengthen the argument made previously[194] that this “slow” relaxation is actually a perpendicular PI normal mode and the mode typically associated with the dielectric PI normal mode in BCP arises from motions parallel to the domain interface. These data suggest that the comparative strengths of these two relaxations by $\Delta\epsilon_n \Delta\epsilon_\alpha^{-1}$ is increased or decreased based on the relative orientations of the lamellae or other domains in bulk. Additionally, the evidence suggests that the dielectric modes of chain motions parallel to the interface have a constant symmetric and asymmetric broadening in the measured dielectric loss as quantified by the $\alpha = 0.76 \pm 0.02$ and $\gamma = 0.36 \pm 0.01$ HN parameters.

Choosing Studies for This Review

It has been well established that the procedural history of block copolymer materials will dictate the relaxation behavior measured by various techniques including DS. The results of sample preparation methods like solvent casting, thermal annealing, etc., establish the degree of phase separation and length-scale of the order that is formed.[94, 95] A whole field of study investigates morphology formed by block copolymers, predicting the various phases and reducing defects in the domain geometries that are produced. With respect to the dynamics of PI containing linear diblock copolymers in different phases, as long as the phase separation occurs the effects will be measured in the dielectric chain relaxation of PI. This is parameterized by the Flory interaction parameter χN , and only polymers that form well separated domains with a well-established interface are considered in the first part of this review($\chi N > 20$). The text argues the orientation of these domains will affect the relative strengths of the relaxations observed and the relaxation shapes. As such, we considered the sample preparation methods in each study to be sure that phase separation was achieved and/or the specific morphologies were characterized by methods like SAXS or TEM. Macroscopically,

isotropic domains are the most prominent occurrences with only a few studies isolating anisotropic dynamics by ordering the domains with respect to the electrodes. These specific studies are also considered and discussed individually in terms of anisotropic dynamics. Anisotropic phase orientations is the statistically most prominent in cylindrical domains, but for all morphologies there is an inherent anisotropy in the dynamics. Therefore, the dynamics are compared in like-phases and different domain orientations will be isolated if applicable.

A majority of the studies included here are of PS-PI diblock copolymers, where the polarization of the counter PS block has a segmental relaxation that is predictable and well understood. The dynamics within the interphase, such as a glassy interphase or rubbery interphase will ultimately contribute to the dielectrically active modes of the PI block. Therefore, the different temperature regimes of the PI normal mode under investigation and the dynamics of the counter-block at those temperatures must be considered and is discussed in separate sections of this review. The contribution of Maxwell-Wagner Sillars interfacial polarization and/or ionic conductivity primarily occurs at $T > 375\text{K}$ and $f < 1\text{ MHz}$. Therefore, the PI chain and segmental dynamics are the only relaxations directly measured from $10^{-1} \leq f \leq 10^7\text{Hz}$ at $T \leq 360\text{K}$ in phase separated PS-PI and PI-PDMS systems, unless the system is near the ODT. For this study we searched through the publication record of dielectric spectroscopy investigations of the PI (high *cis*-1,4 microstructure) Type-A chain relaxation in PS-PI block copolymer systems with accurate predictions and measurement of the well-developed morphology in phase separated systems, systems near the ODT, and for PI in linear diblock copolymers with other chemically dissimilar counter-blocks to ensure individual domains of the two blocks. Particular attention was focused on studies that clearly publish figures with the PI normal mode, and we also chose reports that include PI α -relaxation spectra to more accurately investigate the high frequency wing with fitting both the normal mode and α relaxations at once across a wide frequency range.

We must make some stipulations to the experimental procedure that are required for making such claims. A typical procedure is to prepare a polymer film by melt pressing, then to thermally anneal at $T > T_{ODT}$ under inert atmosphere during *in situ* dielectric measurements until the spectrum stabilizes. This procedure has been shown to favor lamellae that are parallel to the electrodes, but still does not ensure a resulting macroscopically anisotropic orientation throughout. Additionally, for quantitative $\Delta\epsilon$ comparisons, the capacitor geometry must be exactly known with a uniform electric field with a voltage that probes the material in the linear response regime. Otherwise, unintended artifacts of the sample preparation will be observed in the data.

Data analysis was performed by taking a high quality screen-shot of the figure from the .pdf file downloaded from the publisher's website. The digitizer tool of Origin Pro10 was used to select the specific data points in the plot (not picked along a subjective fitting line or data from a model used to simulate the data in the publication). In this way, the more data points in the figure gives higher confidence in the accuracy of the spectral shapes from the digitized plots. From these digitized data, we then fit each set of data with both the reported shape parameters and parameters from our own fitting procedure which let all variables to freely fit. The resulting fits with lowest standard error were used in the meta-analysis (either our fits or the fits with parameters published for that sample). The HN fits used a linear combination of HN functions for each of the relaxations observed in the plot and a $\epsilon''_{\text{conductivity}}$ term if applicable. The error associated with our fit parameters compared to any reported parameters from the literature were accounted for in the averages from the analyzed figures. Additionally, the average value was taken as a weighted average with a value for weight (κ) given to the values for parameters from figures with a larger number of reported data points. For example, κ was determined by taking the number of data points in the plot (Z) and dividing it by both the total number of data points (ζ) and the number of parameters in the fitting ($x = 4$ for one HN function for T_{HN} , $\Delta\epsilon_{HN}$, γ & α , and $x = 2$ for ϵ''_{cond}). To fit in Origin,

the simple average of the reported HN parameters from the literature for α and γ for lamellar PS-PI systems was used to initiate the fitting algorithm. After $\Delta\epsilon$ and T_{HN} were parsed to constant values with α and γ held constant, all parameters left free to fit. The standard error from this fitting was then used in conjunction with the error between our fitting and any reported values, or with a 10% error for data that had no reported parameters.

From these reports of PI in phase separated PS-PI systems, the PI α relaxation shape, which was only used from data in papers that also published PI normal mode data, the HN fit values for the α -relaxation are found in Table 3 above. The α relaxation HN fits for the PI-PDMS systems are found in Table 4 which when averaged with the data in Table 3 give $\alpha = 0.59 \pm 0.05$ and $\gamma = 0.5 \pm 0.2$. The PI normal mode shape parameters for systems with glassy PS block above the ODT are found in Table 5. The PI normal mode shape parameters for systems with glassy PS block below the ODT are found in Table 6. The PI normal mode shape parameters for systems with rubbery PDMS block are found in Table 7. Finally, the weighted average and simple averages of the normal mode relaxation shape parameters for all of the data in Tables 5-7 are found in Table 8.

Conclusions and Outlook

Synthesis methods now afford precise control over the resulting block copolymer morphology[209-211] with the added complication of branched BCP architectures giving rise to interesting geometries, modified molecular dynamics and material properties[212, 213]. The nature of the ensemble average response measured by dielectric spectroscopy makes it difficult to differentiate anisotropic dynamics.[214] However, with the abundance of high quality data published in the literature for various phase orientations in BCP systems, a standardization of the dielectric normal mode relaxation shapes of PI has been described here by employing the widely used HN function.

Table 4: HN parameters for PI α -relaxation in PI-PDMS from the literature

Paper, polymer	alpha	gamma
Lund 2008, 9k 50k	0.51	0.5
Lund 2008, 6k 31k	0.51	0.68
Lund 2008, 4k 23k	0.626	0.556
Alegria 2014, 4k-32k	0.49	0.75
Lund 2013, 4k 4k	0.583	0.3
Lund 2013, 4k 3.5k	0.626	0.35
Lund 2013, 4k 25k	0.54	0.25

Table 5: Meta-analysis data and HN Parameters for ordered PS-PI systems

Author Year polymer	Values for Weighted Avg		Normal mode HN parameters	
	# fit param	total data points	alpha	gamma
Watanabe 1995 11.7-11.6	4	30	0.66	0.37
yao 1991 41.5k-42.5k	8	38	0.6	0.25
Jenczyk 2013 41.8k-49.1k	10	59	0.66	0.31
yao 1991 14.1k-14.9k	8	38	0.65	0.33
Jenczyk 2010 11.4k-10.5k	8	56	0.51	0.41
yao 1991 12.5k-9.5k	8	36	0.55	0.57
Adachi 1997 8k-8k	4	19	0.62	0.165
Koch 1997_data from Stuhn&Wolff	4	66	0.63	0.35
Karatasos 2000 12k12k	10	61	0.6	0.34

Table 6: Meta-analysis data and HN Parameters for PS-PI systems near the ODT

Author Year Polymer	Values for Weighted Avg		Normal mode HN parameters	
	# fit param	Total data points	alpha	gamma
Meins 2012 13k-13k	11	52	0.76	0.35
Meins 2012 17k-15k	11	52	0.79	0.31
Karatasos 1996 8.2k8.2k	10	71	0.76	0.46
Karatasos 1996 6.1k6.1k	10	42	0.72	0.47
Alig 1992 2.8k-2.8k	6	24	0.78	0.26

Table 7: Meta-analysis data and HN Parameters for PI-PDMS

Author Year, Polymer	Values for Weighted Avg		Normal Mode HN parameters	
	# fit param	Total data points	alpha	gamma
Lund 2008, 9k 50k	10	66	0.88	0.33
Lund 2008, 6k 31k	10	69	0.835	0.36
Lund 2008, 4k 23k	10	70	0.94	0.23
Alegria 2014, 4k-32k	10	68	0.86	0.32
Lund 2013, 4k 4k	9	50	0.79	0.395
Lund 2013, 4k 3.5k	9	58	0.84	0.375
Lund 2013, 4k 25k	8	57	0.84	0.33

Table 8: Weighted average and standard deviation of HN Parameters for PI Normal Mode in block copolymer systems

	α	γ
wtd avg->	0.76	0.36
wtd stdev->	0.017	0.011

With the consistent and increased use of the HN function to describe the dielectric relaxations of PI normal modes, a standardization of the experimental data for PI in block copolymer systems is necessary for comparing results from study to study. We show that particular normal modes that are probed for PI chains in relation to the interface have a unique relaxation shape. The overall finding that incorporates sixteen PS-PI BCPs with lamellar morphology from thirteen studies is that the HN shape parameters of the PI normal modes are $\alpha = 0.75 \pm 0.02$ and $\gamma = 0.35 \pm 0.01$ with a $\Delta\epsilon_n$ that largely depends on the degree of long-range order and orientation of the lamellae with respect to the electrode. We argue that the typical normal mode relaxation reflects motion parallel to the interface, and that the observed “slow mode” represents motion perpendicular to the interface that is activated by interfacial defects in accordance with past studies. The changes in the global relaxation behavior have now been summarized for dielectric spectroscopy so that future investigations into these dynamics may be more streamlined and compared more quantitatively from study to study.

Furthermore, while the PI chain is modeled by a coil-like polymer, as opposed to a worm- or rod-like chain, the conformations of the chains under phase separation confinements become more worm-like such that the bending of the chain contour is restricted. The dynamics of this Rouse-like chain confined in a worm like conformation may be modeled in a similar way to Doi and Edward’s description of a chain in a fixed volume box, but by restricting the size of the box in one dimension to $L_z \ll R$ [4]. BCP with non-linear architectures have been shown to have different morphologies at similar block fractions compared to the linear counterparts, and the morphology change may occur without the expected change in packing frustration [215, 216]. The change in packing frustration and with more control over the interfacial geometry that subsequently reduces the distribution in chain stretching energy as shown for the cylindrical morphology (shown in Fig. 32) may be observed for the branched miktoarm star copolymers with asymmetric architectures as will be discussed in Chapter 5 and 6.

In fact, the effect of branching in block copolymer systems has been studied with respect to phase separation. For example, the size of a lamellar domain for the AB linear diblock is known to be ~7-8% smaller than for the A_2B_2 miktoarm star for the same total block molecular weight[217, 218]. Some of the architectural effects on chain conformation, stretching, and interfacial energy have been considered using SCFT, however experimentally perturbing the relaxations and dynamics of these systems and making correlations to these effects is lacking, but is the main focus of Part I.

Summarily, the primary driving force of self-assembly in block copolymers is the enthalpy of mixing. Because the portions of the material that do not mix are literally parts of the same molecule, the positive value for the entropy of mixing must be offset by some other energetic effect. The primary effect that obeys the first law of thermodynamics in block copolymer phase separation is the reduced entropy resulting in increased chain stretching energy. Other effects include conformational entropy of the chains and the surface tension associated with the formation of the interface between disparate domains. This energy balance is expected to change with architecture, and, as will be seen in the following chapters, this change in energy results in altered dynamics measured by BDS.

Chapter 4: Dielectric Relaxations of Polyisoprene in Block Copolymers with Poly(2-vinylpyridine)

- A version of this chapter is being submitted for publication by Thomas Kinsey, Emmanuel Urandu Mapesa, Weiyu Wang, Kunlun Hong, and Joshua Sangoro in *Macromolecules*.

Kinsey, T., et al. *Deconvoluting the Dielectric Relaxations of poly(cis-1,4-isoprene)-b-poly(2-vinylpyridine) block copolymers*. *Macromolecules*, 2021. **XX**(XX): p. XXXX-XXXX.

All of the polymers in this chapter were synthesized and characterized by WW under the guidance of KH. TK prepared and measured all of the samples, and performed the data analysis. TK and EUM wrote the majority of the paper with some of the methods written by KH. All authors contributed edits and revisions. JS provided the funding for this project.

Abstract

For poly(*cis*-1,4-isoprene) (PI) in phase separated block copolymers (BCP), the dielectric chain relaxation is known to be affected by both the thermal state (*i.e.* glassy or rubbery) of the neighboring block and by the domain geometry formed upon self-assembly, primarily from studies with a polystyrene (PS) counter block. While the motions of PS in PS-PI BCP at temperatures $<T_g$ are essentially frozen and not activated by perturbation with electric field at experimental timescales, the localized motions of poly(2-vinylpyridine) (P2VP) β -relaxations are measured and occur at similar temperatures and timescales as the dynamics of the PI block. This study investigates the polarization relaxations of PI four linear PI-P2VP BCPs with constant PI and increasing P2VP block sizes using broadband dielectric spectroscopy and with microstructural characterization by small-angle x-ray scattering. The coincidence of the localized P2VP β -relaxations and global PI chain relaxations in opposing phases are analyzed using Havriliak-Negami functions fit

to the data to reveal that the PI chain relaxations are not altered by the polarization of the P2VP blocks in the glassy state compared to similar PS-PI systems from the literature. Additionally, four 3-arm miktoarm star terpolymers with PS, PI and P2VP blocks are measured and analyzed in a similar way as the linear diblock system to uncover the effect of the miktoarm architecture on the PI dielectric chain relaxations. This fundamental investigation into dielectric relaxations of neighboring blocks in phase separated block copolymers shows that the thermodynamics of phase separation are the primary factors affecting the dielectric relaxations of the PI blocks.

Introduction

Polymer dynamics have been a great focus of mechanical and dielectric research for understanding the timescales of molecular motion that govern their material properties. This is particularly the case for the dynamics associated with the glass transition.[22, 219-221] On the other hand, the polymer chain relaxations which govern elastic properties tend to be more complicated, especially when the aspect of phase separation of block copolymer systems is considered.[118, 145, 188] For mechanical relaxations in block copolymers with a glassy and a rubbery block, there is a relatively clear consensus on the terminal relaxations of the polymer chains in the rubbery state, which change for various geometric morphologies as the fraction of the rubbery chain is altered.[132, 145, 222] However, when it comes to the dielectric chain relaxation in phase separated block copolymers, effects from various morphologies are not fully developed.[93, 133, 144] The dielectric chain relaxations is often studied using poly(cis-1,4-isoprene) (PI), a Type-A polymer, due to the orientation of monomeric dipoles with respect to the backbone.[65, 69, 89] For the homopolymer PI, the dielectric normal modes or chain relaxation are well-studied, and the characteristics of the dielectric spectrum for the normal mode process are well understood and explained through alterations to the Rouse model.[15, 43, 46, 58, 68, 223] In phase separated

systems, the most common approach is to qualitatively discuss changes in the dielectric spectra measured for PI chains in block copolymers, primarily with the glassy counter-block polystyrene (PS), by generally evoking a balance between some spatial and thermodynamic constraints.[92, 119, 126]

It is well established that the dielectric relaxations and dynamics of individual blocks at different length- and time-scales are dependent on both the state of each blocks (glassy, rubbery, or crystalline) and the geometry of the domains formed by phase separation.[158, 174, 224] These types of experiments are made possible by the wide difference in the temperature and relaxation timescales that are associated with the dynamic glass transition of the PS and PI blocks and also the dielectrically active PI normal mode relaxation has allowed many scientific questions concerning the dynamics of block copolymers to be investigated and answered. While this wide difference in temperatures and timescales of the glassy states is useful, there are questions that remain for the dynamical effects of blocks in neighboring domains. This study focuses on the dynamics of poly(*cis*-1,4-isoprene)-*b*-poly(2-vinylpyridine) (PI-P2VP) diblock copolymers to determine if the relaxations at different length scales of each block that occur at similar timescales are truly additive to the dielectric spectrum or if the polarization of one block effects the dielectric relaxation of the neighboring block. In other words, are there non-zero cross-correlations of polarization relaxations at similar timescales that are probed at different lengthscales among the phase separated blocks? This has been assumed in past studies of PS-PI systems for the PI normal mode and the PS α relaxation, but has not been truly ruled out due to possible changes in the PI normal mode due to softening of the interface above the T_g of the PS block.[194]

The miktoarm star copolymer has been identified as a potentially useful tool for applications ranging from drug delivery to advanced nanolithography [213, 225, 226]. Many reports have shown that with the miktoarm star terpolymer architecture, the geometric morphologies formed are more complex and unique compared to

any linear system [227-229]. Specifically, these systems form uniquely one-dimensional domain boundaries whereas the linear triblock terpolymers and other linear diblock copolymers have two-dimensional boundaries between domains [230, 231]. While the miktoarm star terpolymer with arms of PS, PI and P2VP have been well characterized with respect to the phase structures that are formed, the motions of the blocks have not been investigated. Additionally, with the effects of the morphology on the dynamics in diblock copolymer systems covered in Chapter 3, the role of the molecular architecture on the dynamics of the polymer chains contained in the unique phase separated domains formed by these systems are investigated here.

The discussions of the results in this study are within the context of PI segment and chain relaxations at and above the PI block T_g , but below the T_g of the P2VP block (and/or the PS block) at which a dielectric P2VP β -relaxation is measured at similar timescales as the PI chain (kHz region). Two methods, one analytical and one experimental, are used to deconvolute these relaxations from the dielectric spectrum in the linear PI-P2VP diblock systems. The experimental approach involves chemically altering the environment of the pyridine segments by selectively solvating Li^+ cations into the domain which has been shown to both alter and localize polymer dynamics and sharpen the phase separated domain interfaces.[232-236] The analytical approach employs the time-temperature superposition of relaxation and the widely Havriliak-Negami fitting function to describe and parse the data. These results are compared to the similar PS-PI systems from the literature where PS does not have a dielectric signal near the timescales of the PI block. This study finds that the P2VP β -relaxation and the PI chain relaxation at different length scales and within different domains are quantitatively additive to the dielectric spectrum and can be deconvoluted using the empirical Havriliak-Negami function. We also find that the shape of the PI chain relaxation follows the qualitative trends reported for PS-PI systems with similar morphologies. Finally, the effects of the miktoarm star terpolymer architecture are

considered for PSPIP2VP systems as compared to the linear PS-PI from the literature and the PI-P2VP systems in this study.

Materials and Methods

For this study, four PI-P2VP block copolymers were synthesized by anionic polymerization with lithium counter cation in distilled benzene by previously published methods to ensure high *cis*-1,4 microstructure of the PI block. The polymer characteristics measured by standard NMR and GPC methods are found in Table 9 (and are also shown in the Introduction to Part I). The GPC curves were calibrated with respect to polystyrene standards, and thus are acceptable estimates of the PI and P2VP blocks. Following purification, the polymers were handled under conditions that minimized light and ambient air exposure to ensure the PI block did not degrade or oxidize during sample preparation. See the section following the Results and Discussion for details on the miktoarm star terpolymers.

Sample preparation of neat polymers for both x-ray and dielectric spectroscopy was performed by melt pressing the polymer at 120°C for 10min under inert conditions between Teflon into 200µm films. After cooling to room temperature, the Teflon was removed, and the films were placed either directly onto the 10mm diameter stainless steel electrodes with 200µm silica rod spacers for dielectric experiments or thermally annealed at 150°C for at least 48h under inter atmosphere then cooled and sandwiched between Kapton tape for x-ray scattering measurements. The salt doped samples were prepared by dissolving the polymer at 5wt% in HPLC grade THF purged with N₂ for 30 minutes, and by dissolving LiClO₄ to dry methanol to a ~300mg/mL concentration. The salt/methanol solution was added volumetrically to the polymer/THF mixture to result in a 10:1 ratio of nitrogen in the P2VP repeat units to Li⁺ cation, and stirred overnight at 40°C. Then, 0.5g of each mixture was cast onto Teflon disks under N₂ atmosphere and heated to ~80°C for 20h and cooled to room temperature over the span of 5h.

Table 9: Diblock Copolymer Characteristics for Chapter 4

NAME	Total Molecular Weight			PI Block			P2VP Block		w% of P2VP		(PI volume fraction) ^a
(PI-P2VP)	M _n	M _w	PDI	M _n	M _w	PDI	M _n	M _w	GPC	NMR	Φ_{PI}
20k-5k	23,200	24,800	1.07	19,000	20,000	1.05	4,200	4,800	18.0%	12.2%	0.83
20k-10k	31,600	33,500	1.06				12,600	13,500	39.9%	32.1%	0.72
20k-15k	35,700	38,200	1.07				16,700	18,200	46.8%	40.0%	0.63
20k-20k	40,600	43,800	1.08				21,600	23,800	53.2%	42.0%	0.56

^aP2VP density=1.12 g/cm³

^aPI density=0.89 g/cm³

The films on the Teflon disks were then placed into a high vacuum oven ($<10^{-8}$ mbar) at 150°C for 2h to drive off remaining solvent and to thermally anneal the $\sim 200\text{-}250\mu\text{m}$ samples. The resulting salt doped samples were removed from the Teflon and placed onto the electrodes or between Kapton tape.

The broadband dielectric spectroscopy (BDS) measurements were performed using a Novocontrol Alpha-A analyzer at frequencies from $10^{-1}\text{-}10^6$ Hz with an applied field of 0.1V. Temperature was controlled by a liquid N_2 Quatro cryostat ($\pm 0.1\text{K}$). Prior to starting the measurement, the $200\mu\text{m}$ sample was thermally annealed in the cryostat at 420K and measured over time until a constant permittivity spectrum was achieved ($\geq 16\text{h}$). The sample was then cooled rapidly to 300K then measurements were taken upon cooling and subsequent heating in 5K steps from 220 - 380K. The microphase-separated morphology adopted by the copolymers was characterized using a Ganesha small angle x-ray scattering (SAXS) instrument, which is comprised of a 50kV Cu Xenocs Genix ULD point source and a $170\mu\text{m}$ pixel, 20Hz Dectris Pilatus 300k detector. The scattering profile of a double layer Kapton tape was measured and directly subtracted from the sample scattering profiles as a background. Kapton blanks were measured between each sample measurement to ensure that there was no drift in source intensity.

Results and Discussion

The self-assembled microstructures and dielectric relaxations are investigated for four block copolymers in this study contain a 20kg/mol PI block with a 5, 10, 15 or 20 kg/mol counter block. The result of solvating the Li^+ salt into the P2VP block to suppress the localized motions of P2VP segments will be discussed later. First, the morphologies formed were measured using SAXS as shown in Figure 37, where the peak positions are noted in the plot. The polymer with the lowest molecular weight P2VP block (5kg/mol) forms disordered spheres. The polymers with the next largest molecular weight P2VP blocks (10kg/mol and

15kg/mol) form cylindrical P2VP domains and the polymer with symmetrical block weights (20kg/mol P2VP) forms P2VP cylinders and lamellae consistent with previous works.[237, 238]

The frequency dependent dielectric loss ϵ'' spectra of these four polymers are shown in Figure 38 from 220 to 350K where all of the observed relaxations move toward higher frequency with increasing temperature. The PI α -relaxation is seen at the lowest temperatures for all polymers (220K-250K), but this relaxation becomes a high-frequency shoulder to a strong, broad relaxation for the lower ϕ_{PI} polymers as temperature increases (Figs. 38b-d). This strong, broad relaxation increases in intensity as temperature increases for all polymers and is identified as the β -relaxation of the P2VP block associated with local “cage-like” motions of the side group dipole that is formed within the monomeric heterocycle.[28, 239, 240] This P2VP β -relaxation has been observed in several experimental studies and is measured for P2VP in the glassy state. [127, 241-244]

Finally, in Figure 38a for the highest ϕ_{PI} polymer there is a low frequency process that is observed clearly at $T \geq 250K$. This is the typical PI normal mode or chain relaxation that is expected for a 20kg/mol PI block. However, in Figures 38b-d, this PI chain relaxation is not clearly observed at $T \geq 250K$ toward low frequencies. Similar to the PI α -relaxation becoming a high frequency shoulder to the strong polarization of the P2VP β -relaxation at higher temperatures, the loss intensity of the PI chain relaxation appears as a low frequency shoulder in the lower ϕ_{PI} polymers. The PI chain relaxations for these three polymers are expected to be broadened and reduced in intensity relative to the 20k-5k polymer due to morphological changes, and therefore, these results are expected.

In order to further examine this “buried” PI chain relaxation in more detail, a first approach is to analytically use the principle of time-temperature superposition (TTS).

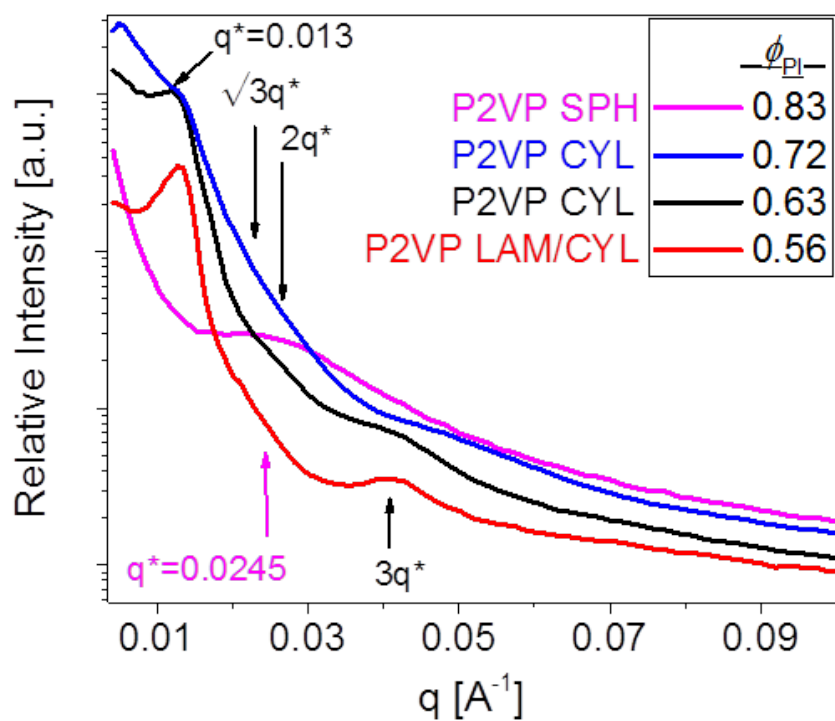


Figure 37: SAXS profiles of the block copolymers in this study. The q^* values are noted in the plot and higher order peak locations for the $q^* = 0.013$ peak are displayed.

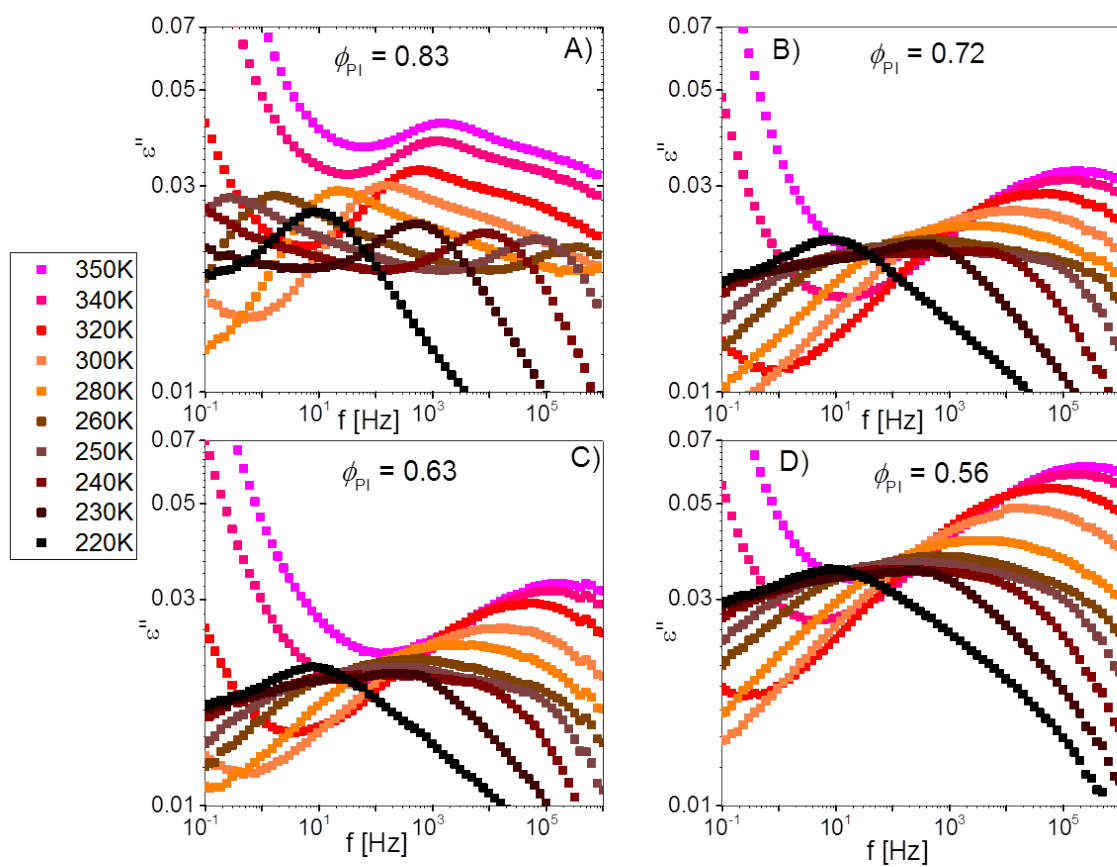


Figure 38: The dielectric loss data at several temperatures for the neat 20k-5k polymer (A), 20k-10k polymer (B), 20k-15k polymer (C) and 20k-20k polymer (D).

This TTS analytical approach shifts the frequencies of the dielectric spectra at each temperature by a temperature dependent shift factor a_T to create a representative master-curve that is typical for measuring the dielectric response of these types of materials.

The a_T with a $T_{ref} = 270K$ for linear PS-PI block copolymers have been consistently reported to be accurate for different molecular weights and morphology if the PI relaxation shape is temperature independent and the relaxation rates of the PI α - and chain relaxations are well separated in frequency.[46, 92, 245] The difference in the temperature dependence of the PI chain and α -relaxations, however, are such that the resulting mastercurves are only representative of the ϵ'' spectra at T_{ref} . The dielectric spectra from Figure 38 are then shifted by a_T at each temperature, and the resulting mastercurves are shown in Figure 39.

In Figure 39, the frequency axes of these mastercurves are normalized by the frequency of maximum loss of the PI α -relaxation ($f_{\alpha-PI}$) at 270K, and vertical lines in the figure signify this normalized rate and normalized the chain relaxation rate at 270K for the $\phi_{PI} = 0.83$ polymer (*i.e.* these lines are based on PI α - and chain relaxations in Fig. 38a for comparison with Figs. 39b-d). The expected smooth relaxation spectrum that is produced by this type of analysis for PS-PI block copolymers is not observed for these PI-P2VP polymers. This is likely due to a difference in temperature dependences of the β -relaxation in glass formers (typically Arrhenius-like) [246] compared to the PI α and chain relaxations (which follow the Vogel-Fulcher-Tammann equation). Furthermore, TTS was shown to not be a valid approach to analyze the P2VP dielectric spectra at $T < T_g$ due to intensity changes in the β -relaxation.[241] This failure of the TTS makes comparing the spectral shapes of these relaxations difficult without further analysis.

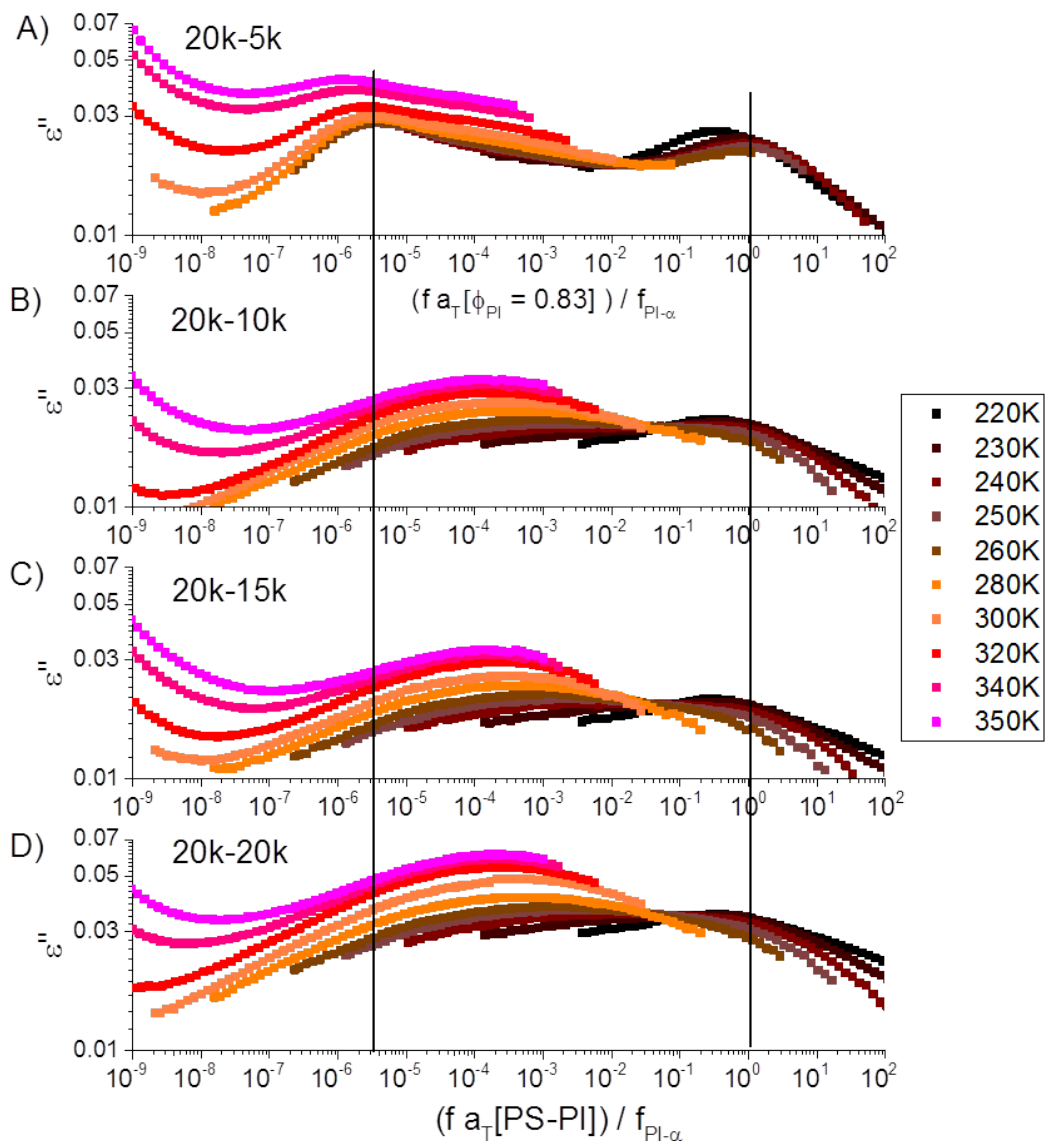


Figure 39: Pseudo mastercurves of the neat 20k-5k polymer (A), 20k-10k polymer (B), 20k-15k polymer (C) and 20k-20k polymer (D). The data in (A) are shifted by the a_T factors that are representative of the 20k-5k polymer, whereas the a_T factors for the PS-PI systems from the literature are used for (B-D). These mastercurves show that the P2VP β -relaxation contribution does not allow the smooth curves of the PI relaxations that are observed for PS-PI systems.

In several past studies, the dielectric relaxation shapes and mean relaxation rates of the P2VP β -relaxation under various physicochemical environments and the PI α -relaxation in phase separated block copolymer systems are reported based on analytical fitting to the complex dielectric function with the empirical Havriliak-Negami function (HN).[127, 241-244, 247] The HN function is shown in Eqn. 79 where τ_{HN} is the characteristic relaxation time, $\Delta\epsilon_{HN}$ is the relaxation strength and α and γ are shape parameters for symmetric and asymmetric broadening of the typical Debye relaxation.

$$\epsilon^*(\omega) = \Delta\epsilon_{HN} [1 + (i\omega\tau_{HN})^\alpha]^{-\gamma} \quad 79$$

Also, based on the arguments by G. Phillies, one would expect that if there are no cross-correlations between the polarization of the localized P2VP segments and the PI chain and monomeric dipoles, then a direct subtraction of an accurate representation of the polarization response of P2VP relaxations from the dielectric spectra would resolve the PI chain and segmental processes.[248] Guided by these studies, we have performed a deconvolution of the relaxation spectra starting with the $\phi_{PI} = 0.83$ polymer by analytically fitting the spectra with the reported relaxation shapes of the PI α - ($\alpha = 0.65$, $\gamma = 0.55$) and P2VP β -relaxation ($\alpha = 0.21$, $\gamma = 1$)[127, 241, 243, 249] then letting the shape parameters for the PI chain relaxation to freely fit using a linear combination of three HN functions at each temperature.

As an alternative approach, we also used an experimental method of adding high concentrations of LiClO₄ (10:1 ratio of N:Li⁺, see Materials and Methods for details) to the P2VP block which has been shown to change the polarization response associated with the P2VP β -relaxation at increasingly higher concentrations: increasing rates with a higher activation energy, decreasing dielectric strength, decreasing interchain scattering peak intensity.[127] Other lithium salts and chemical dopants have also been shown to alter dynamic

properties of P2VP and other localized polymer relaxations by decreasing the molar volume of side groups contributing to these dynamics.[247, 250-252]

To compare these two deconvolution approaches, the dielectric spectra of the 20k-5k polymer ($\phi_{PI} = 0.83$) at 260K, measured with and without the addition of salt are shown in Figure 40 (solid symbols). At first glance, the peak rates of the PI α - and chain relaxations do not appear to be altered by the addition of lithium, but there is a reduced ϵ'' intensity at intermediate frequencies for the salt doped system. The dashed lines in Figure 40 show the three HN fitting functions, which fit well to the three relaxations in the spectrum for the neat polymer. Based on previous reports that show the addition of salt is preferentially solvated by the P2VP block[232-234], the shapes of the PI α - and chain relaxation are not expected to change due to the presence of the LiClO₄. The HN functions fitted to these two processes (with $\alpha = 0.77 \pm 0.03$ and $\gamma = 0.73 \pm 0.1$ for the PI chain relaxation for both neat and salt doped systems) are then subtracted from the spectrum.

This analysis reveals a process that resembles the typical P2VP β -relaxation for both systems, but with a reduced intensity and an additional faster relaxation shoulder with the addition of salt (see open symbols in Fig. 40). This subtracted data for the salt doped system (open black squares in Fig. 41) is then fit with two HN functions: one with the P2VP β -relaxation shape parameters, the other left to fit freely. The fits show that the β -relaxation intensity is decreased, and the high frequency shoulder is relatively narrow with weak intensity. The rates of all of these relaxations for the 20k-5k polymer with and without LiClO₄ are calculated using $\omega_{max} = 2\pi T_{HN}^{-1} [\sin(\pi\gamma/2(\alpha+1)) / \sin(\pi\gamma\alpha/2(\alpha+1))]^{-\gamma}$ and the HN fitting parameters. These rates along with the rates for the P2VP α -relaxation observed at $T \geq 350K$ are plotted against inverse temperature in Figure 41. Additionally, the SAXS profile for the salt doped system displays stronger ordering but maintains spherical P2VP morphology (see Fig. 42).

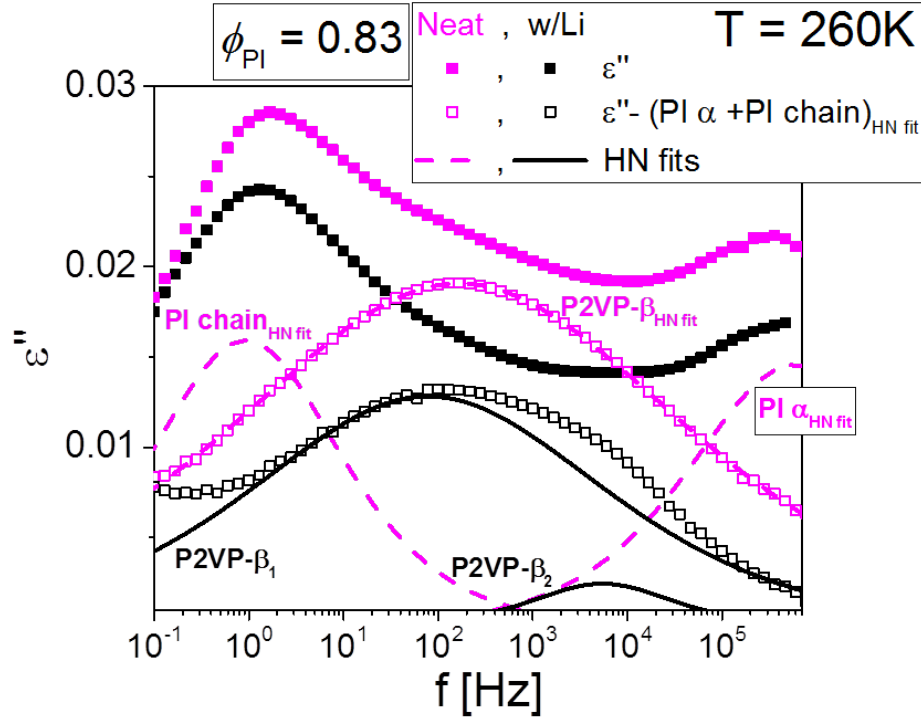


Figure 40: The dielectric loss data for the neat (solid pink) and salt doped (solid black) 20k-5k polymer at 260K. Open symbols are the result of subtracting the PI α - and chain relaxation fits (dashed pink lines) from the spectra. The dashed lines represent HN fits to the data for PI relaxations and P2VP β -relaxation for neat polymer. The solid lines are the HN fits to the P2VP β_1 - and β_2 - relaxations in the subtracted data for the salt doped polymer.

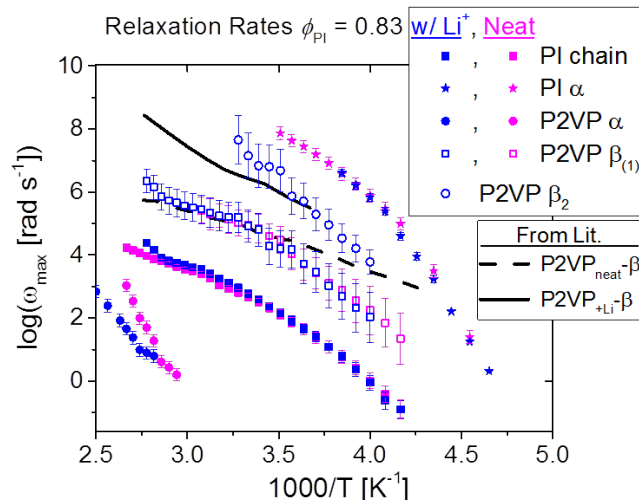


Figure 41: The rates of maximum loss for the PI relaxations and P2VP relaxations for the neat (pink) and salt doped (blue) 20k-5k polymer. Dashed and solid lines are the P2VP β -relaxation rates for the neat and salt doped homopolymer, respectively, from the literature.

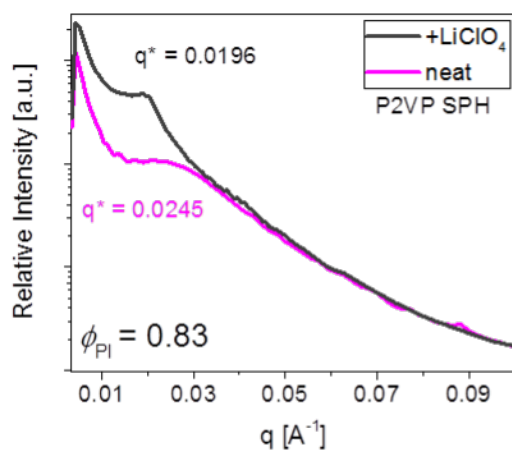


Figure 42: SAXS profile for the 20k-5k polymer with and without Lithium.

From the analytical deconvolutions and experimental suppression of the P2VP β -relaxation by addition of LiClO_4 , it is revealed that for the 20k-5k polymer the PI chain relaxation rates and the P2VP β relaxation rates are independent of the addition of salt (see Fig. 41). At higher temperatures, lower frequencies in Figure 41, the P2VP α -relaxation rates are slowed after the addition of salt. The additional weak process at higher frequencies to the β -relaxation revealed from the analysis is identified as P2VP- β_2 in Figure 40. This is likely the localized polarization response of P2VP monomeric units whose relaxations have become faster due to the salt addition. When examining the rates of the P2VP- β_2 relaxation, they are determined to be comparable to rates reported in a previous study which are reproduced as the solid line in Figure 41.[127] Therefore, with the discrete P2VP spherical phases, we attest that P2VP β_2 -relaxation is representative of P2VP domains that contain higher amounts of Li salt, which leave some P2VP phases that do not contain or contain less solvated salt.

The neat-like phases in the Li^+ doped 20k5k polymer with discrete P2VP phases result in the typical β -relaxation but also a β_2 - relaxation at faster timescales. This is strengthened by comparison of the SAXS profiles of the salt doped and neat polymer in Figure 42. In Figure 40, dielectric relaxation strength $\Delta\epsilon_{\text{HN}}$ of the β -relaxation is reduced for P2VP+ Li^+ compared to the neat system, but otherwise the shapes of the PI relaxations are unchanged. These results show that the PI chain and segmental relaxations in the 20k-5k polymer are not altered with the addition of salt.

Next, the dielectric spectra of the 20k-20k block copolymer ($\phi_{\text{PI}} = 0.56$) is presented using the analytical perspective described above and by experimentally doping with 10 N:1 Li^+ salt. This salt addition causes a clearer scattering profile of lamellae phases for the 20k-20k polymer (see Fig. 43). A representative ϵ'' master curve of the salt doped $\phi_{\text{PI}} = 0.56$ polymer is shown in Figure 44b compared to that of the neat polymer in Figure 44a (same data as Fig. 39d).

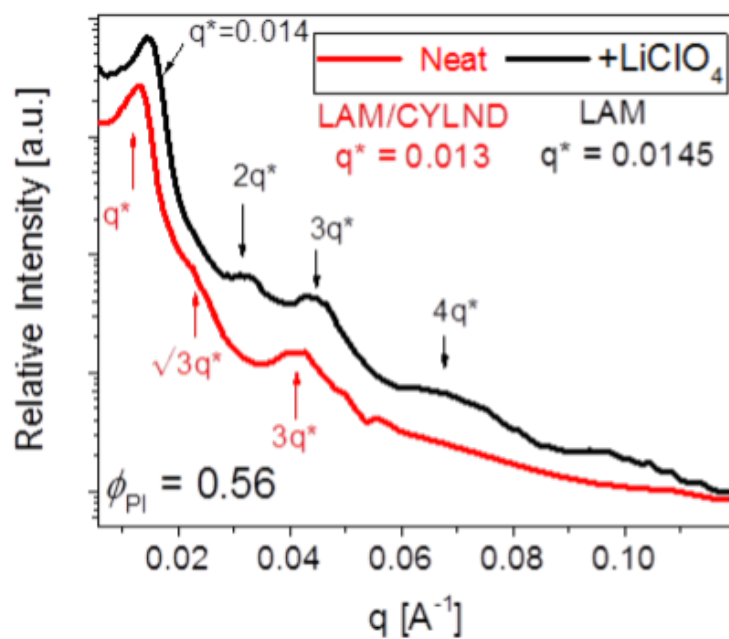


Figure 43: SAXS profile for the 20k-20k polymer with and without Lithium

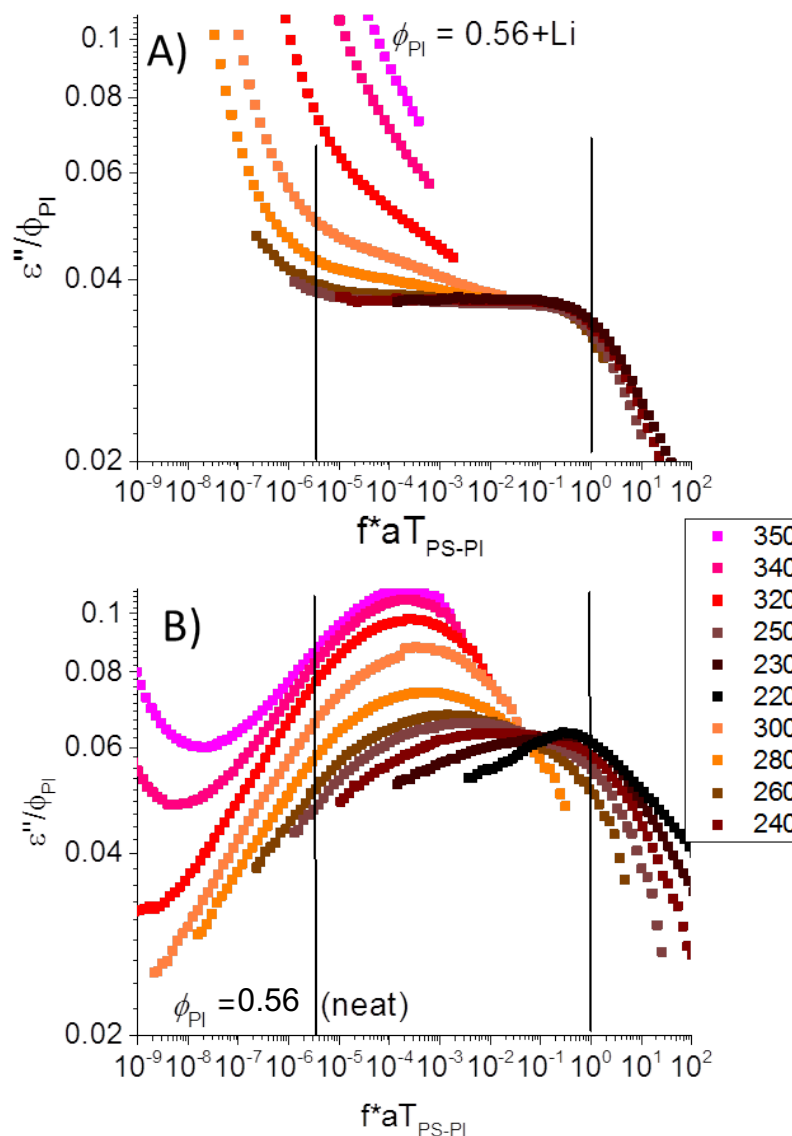


Figure 44: The mastercurve ε'' data normalized by ϕ_{PI} and based on the shift factors for the PS-PI systems from the literature for the salt doped 20k-20k polymer (A) and neat 20k-20k polymer (B). The frequency axis is also normalized by the $f_{PI-\alpha, max}$. The conductivity contribution at low frequencies in (A) causes an inability to observe other processes hidden beneath this strong dispersion. The solid lines are the relative rate of maximum loss for the PI α -relaxation at high frequencies and for the PI chain relaxation at lower frequencies.

There is a strong dispersion toward low frequencies for nearly all of the temperatures measured with the addition of LiClO_4 . This was also observed for the two remaining block copolymers with the addition of salt and occurs due to the continuous P2VP domains which allows for paths of long-range ion conduction contribute to the loss spectra. This low frequency dispersion isn't observed for the salt doped 20k-5k system because the P2VP domains are distinct spheres within a matrix of PI blocks which restricts this conducive polarization. An attempt was made to analytically deconvolute the relaxations from these data, but no PI chain relaxation could be deduced. Only a P2VP β - and β_2 -relaxations could be realized through a relatively subjective perception of peak maxima in different representations of the dielectric spectra. See Figure 45 for the temperature dependent rates that were handpicked from the $\text{Tan}\delta$ and ϵ''_{der} representations of the dielectric data (not shown). We conclude that the addition of Li^+ salt to suppress the local pyridine polarizations may be used as an experimental tool to realize the shape of relaxations in the neighboring PI domain, but is not a reasonable approach when the morphology allows for long range ion hopping.

An aspect that is particularly notable, however, are the rates that are observed near the timescales of the neat P2VP- α relaxation on the addition of salt. For the 20k-20k polymer with Li^+ , these rates are taken from where the dielectric storage and loss crossover and are faster than the neat P2VP- α relaxation (*c.f.* Fig 45). This is contrasting to slower rates near those observed for the P2VP α -relaxation for the 20k-5k polymer with Li^+ (*c.f.* Fig 41). We expect that this process in the salt doped 20k20k polymer is not actually the α -relaxation of P2VP segments, but, based on other studies that observed segmental relaxations that are slowed with the addition of salt, it is a Maxwell-Wagner-Sillars interfacial polarization process and the α -relaxation is not observed.[242, 253] Going forward, only the analysis of the dielectric spectra of the neat polymers are discussed.

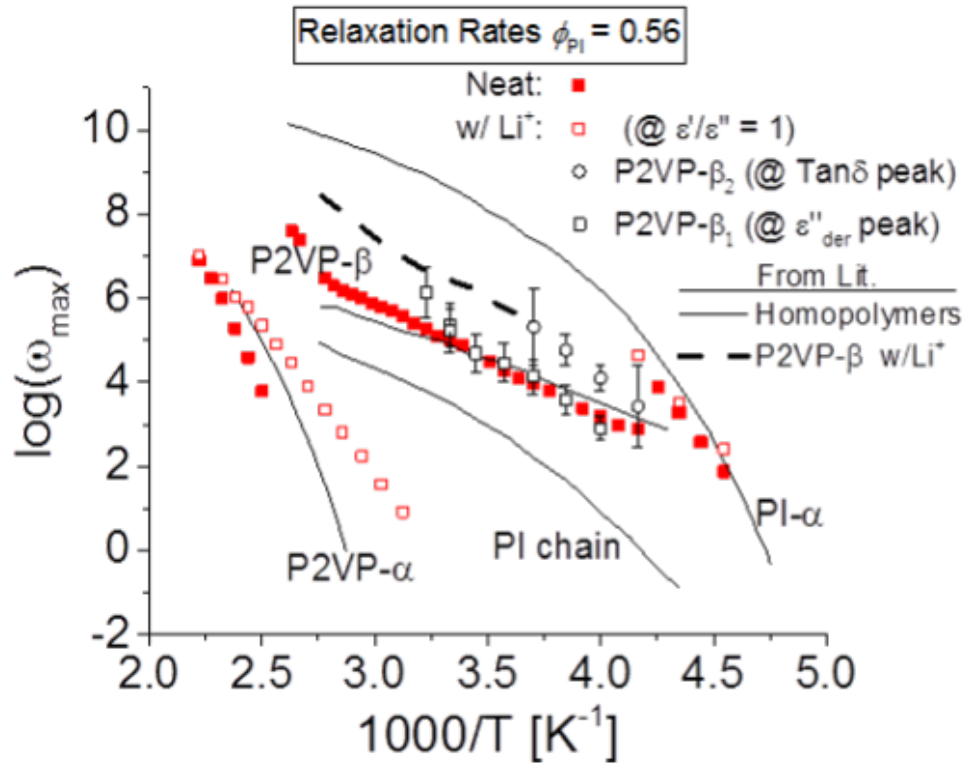


Figure 45: Relaxation rates for the 20k20k polymer with and without lithium. The rates for the doped polymer were not fit with the HN function but were determined by selecting the data point for a peak in the $\tan\delta$ or ϵ''_{der} plots, or from the frequency where the material is no longer lossy (*i.e.* the crossover frequency of the storage and loss permittivity values, $\epsilon'/\epsilon'' = 1$). The solid lines represent the rates for the homopolymers from the literature as noted on the plot.

In Figures 46a-c, the ϵ'' is normalized by the ϕ_{PI} , and then normalized by the frequency of maximum loss of the P2VP β -relaxation ($f_{P2VP-\beta,max}$) at each temperature. The HN fitting parameters used to fit the P2VP β -relaxation of the 20k-5k polymer ($\phi_{PI} = 0.83$) were then used to subtract this process from the ϵ'' spectra to reveal the data in Figures 46d-f. The revealed relaxation shapes are qualitatively similar to those observed for the PI α - and chain relaxations in PS-PI systems and exist at similar rates as shown in the open symbols in Figures 46d-f. The PI chain relaxation qualitatively broadens for the 20k-15k and 20k-20k systems compared to the lower ϕ_{PI} sample. This is expected for the morphological differences across these three polymers.

Additionally, the non-normalized ϵ'' spectra at each temperature were fit to show the temperature dependence of the HN parameters for the P2VP β -relaxation in these polymers. These data are displayed in Figure 43 where the shapes of the β relaxation are constant, except for an increased dielectric strength for the 20k-10k polymer. This increased dielectric strength for the P2VP β -relaxation was reported for isotactic P2VP compared to atactic P2VP and was attributed to a higher internal energy required for the local relaxation mechanism due to restrictions imposed by the polymer backbone conformation in the isotactic polymer.[254] In our block copolymers, the P2VP blocks are atactic, however, the changes in morphology are such that similar thermodynamic restrictions to chain conformations may be imposed. Furthermore, the 20k-10k polymer has a less well-defined morphology (*c.f.* Fig. 37) which may cause the P2VP side groups in segments near the interphase to be less free to rotate than in well-defined P2VP domains.

Next, the data in Figures 46d-f and at other temperatures (220K – 300K) are combined and the frequencies are shifted by the a_T of the 20k-5k polymer to reveal mastercurves of the PI relaxation data with the P2VP β -relaxation subtracted (see Fig. 47).

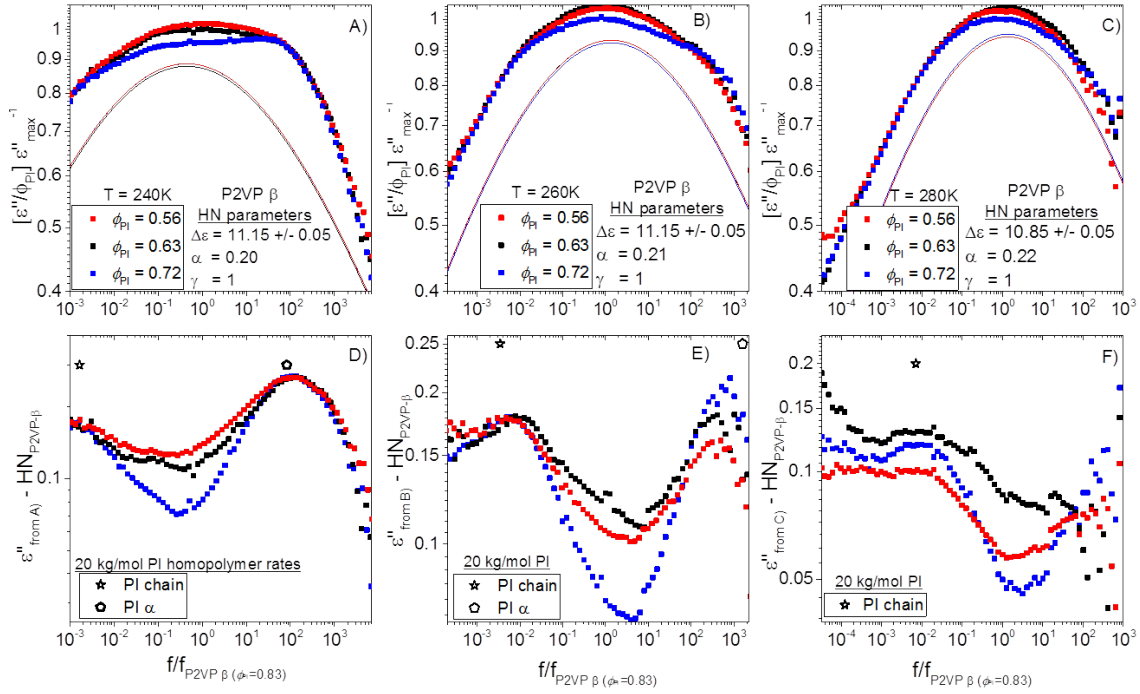


Figure 46: Dielectric loss data at 240K (A), 260K (B) and 280K (C) for the 20k-10k, 20k-15k and 20k-20k polymers normalized by the PI volume fractions. The solid lines in (A-C) are the HN fits for the P2VP β -relaxation based on the parameters shown and Eqn. 79. These fits are subtracted from the data in A, B and C to reveal the data in D, E and F, respectively. The open star and pentagon symbols in (D-F) are the rates of the PI α and chain relaxations for a 20kg/mol homopolymer reduced by a factor of 4. All frequencies are normalized by the rate of maximum loss for the P2VP β -relaxation from the neat 20k-5k polymer (c.f. Fig. 41).

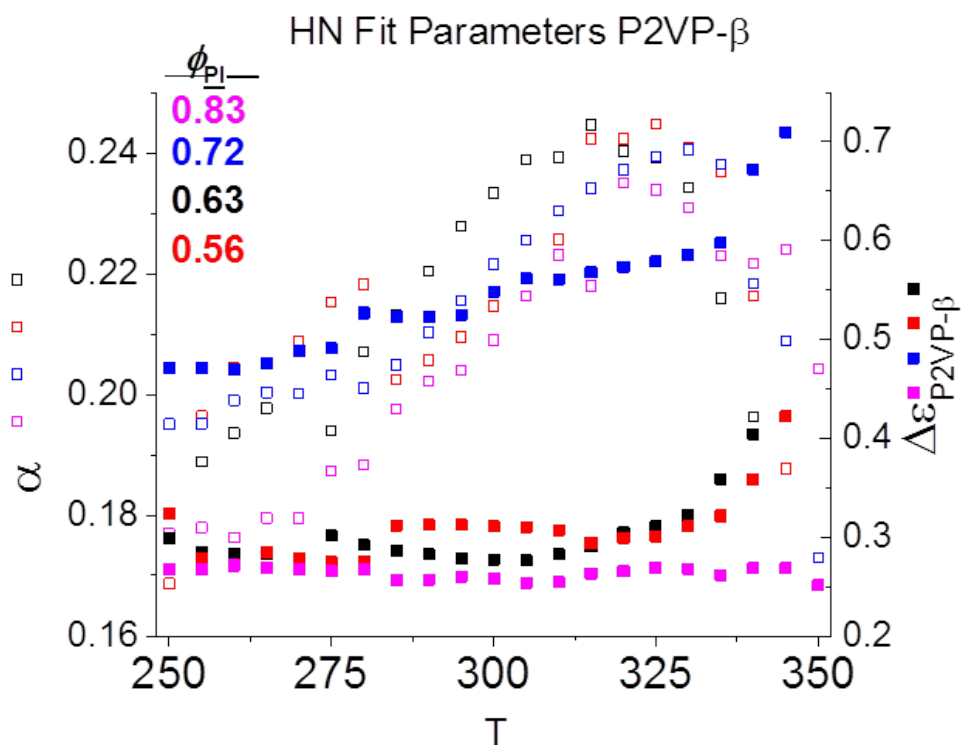


Figure 47: The resulting fitting parameters ($\gamma = 1$) for the P2VP β -relaxation in the neat block copolymers at each temperature. These fitting parameter data are from fittings to each temperature with constrained HN fits to the PI α - and chain relaxation in the subtracted data in Figs. 46d-f. These data show that the dielectric spectral shape of the P2VP β -relaxation is relatively independent of morphology, and narrows similarly as temperature increases (increase in α with increase in T) for all polymers. The shape and strength are shown to be independent of the P2VP content, with the exception of an increased dielectric strength for the $\phi = 0.72$ polymer. See main text for details.

The PI α - and chain relaxations in Figures 47a-d are fit with a linear combination of two HN functions with a low frequency conductivity contribution ($\epsilon''_{\alpha}(f) = \sigma_0 (\epsilon_0 2\pi f)^{-1}$, where ϵ_0 is the vacuum permittivity and σ_0 is the dc conductivity). The HN fitting parameters for the high frequency PI α -process and the low frequency chain relaxation are displayed in the figures and agree with the relaxation shapes for the PI block as reported in Chapter 3. The ratio of the $\Delta\epsilon$ for the PI α and chain relaxations are noted in the caption of Figure 47. For the PI homopolymer this ratio is ~ 1.25 for entangled systems and unity for lower molecular weights [46].

For PI in PS-PI, the $\Delta\epsilon_n \Delta\epsilon_{\alpha}^{-1}$ ratio is often reduced for less well-defined morphologies and a reduced number density of dipoles contributing to the chain relaxation, but the value can approach 1.25 for more well defined morphologies. This is also the case for these systems where the 20k-10k polymer has the least well-defined domains. (We note that this analysis is of course only within instrumental error, particularly for subtracting such an intense polarization response to deconvolute the presence of a much weaker relaxation.)

The analytical results in Figures 48a-d show that the P2VP β -process does not alter the temperature dependent shape of the PI chain relaxation. This is important due to the differing temperature dependences in the polarization response of the P2VP β -relaxation and the two relaxations of the PI block. If the polarized P2VP side groups influenced the polarization response of the monomeric dipoles in the PI block differently at each temperature, it would be expected the relaxations of the PI block would deviate accordingly with respect to the differences in the relaxation rates. Thus, the occurrence of the monomeric units of P2VP to polarize does not affect the polarizations of the neighboring PI block at different length-scales as long as the states of each block (glassy or rubbery) are unchanged.

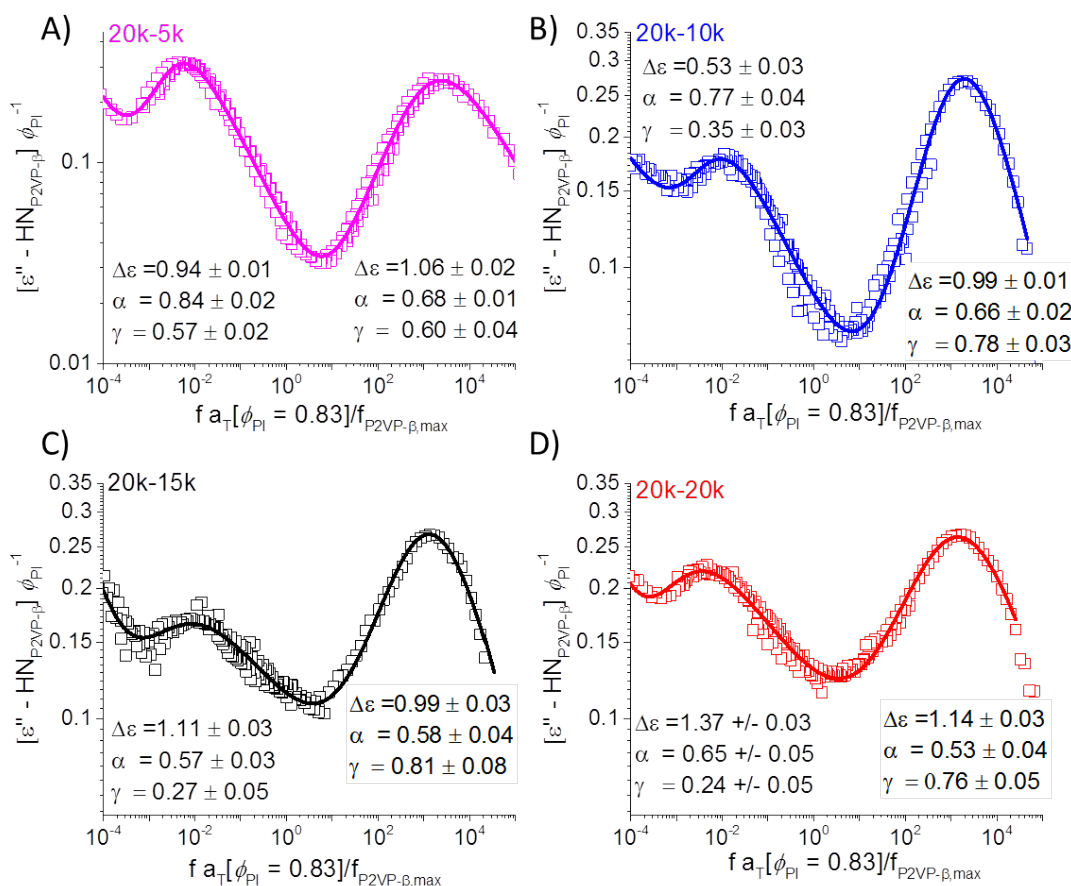


Figure 48: The dielectric α and chain relaxations for the PI blocks at high and low frequencies, respectively for each polymer in master curve representations with the P2VP β -relaxation subtracted from the spectra. The HN fit parameters to these mastercurve data are shown in each plot. The relative strengths of the chain relaxation to the α -relaxation ($\Delta\epsilon_{\text{chain}}/\Delta\epsilon_{\alpha}$) are 0.88 (A), 0.54 (B), 1.12 (C) and 1.20 (D). See main text for details.

Lastly for the linear diblock PI-P2VP systems, the temperature dependencies for frequencies of maximum loss of the PI α - and chain relaxations along with those for the P2VP α - and β -relaxations are shown in Figure 49. All of these relaxations follow the expected temperature dependence and occur at the timescales that are expected as previously explained. That is, except for the P2VP β relaxation with its Arrhenius temperature dependence having a slightly increased activation energy. Past experiments on the sub- T_g dielectric relaxations for polymers under various physicochemical conditions have shown that the thermal activation energy may be increased due to conformational requirements of the chains within the domains.

Dynamics of PS-PI-P2VP Miktoarm Star Terpolymers

The original intent of this study was to specifically identify the effects of the ABC miktoarm star terpolymer architecture on the dielectric chain relaxation of PI in the PSPIP2VP polymers based on the analytical procedures used for the PI-P2VP systems above. All of the miktoarm samples were prepared for measurement in the same way as for the PI-P2VP polymers above. The data for the PSPIP2VP miktoarm star copolymers will now be considered and discussed.

In Figures 50A and 50C, the SAXS data are presented for the four PS-PI-P2VP miktoarm star terpolymers. All of these polymers contain a 10kg/mol PS block, a 10kg/mol PI block and varied P2VP block molecular weights (18 kg/mol, 35 kg/mol, 48 kg/mol and 87 kg/mol) to give the volume fraction ratios shown in Figure 50D. Based on X (the ratio of the P2VP and PI volume fractions shown in Fig. 50B), the lowest P2VP volume fraction system is the only polymer that forms discrete P2VP phases, and based on the results above for PI-P2VP systems, addition of LiClO_4 was only attempted for the 10k10k18k system. The addition of salt results in a change from lamellae phases to cylindrical based on the SAXS profile in Figure 50C.

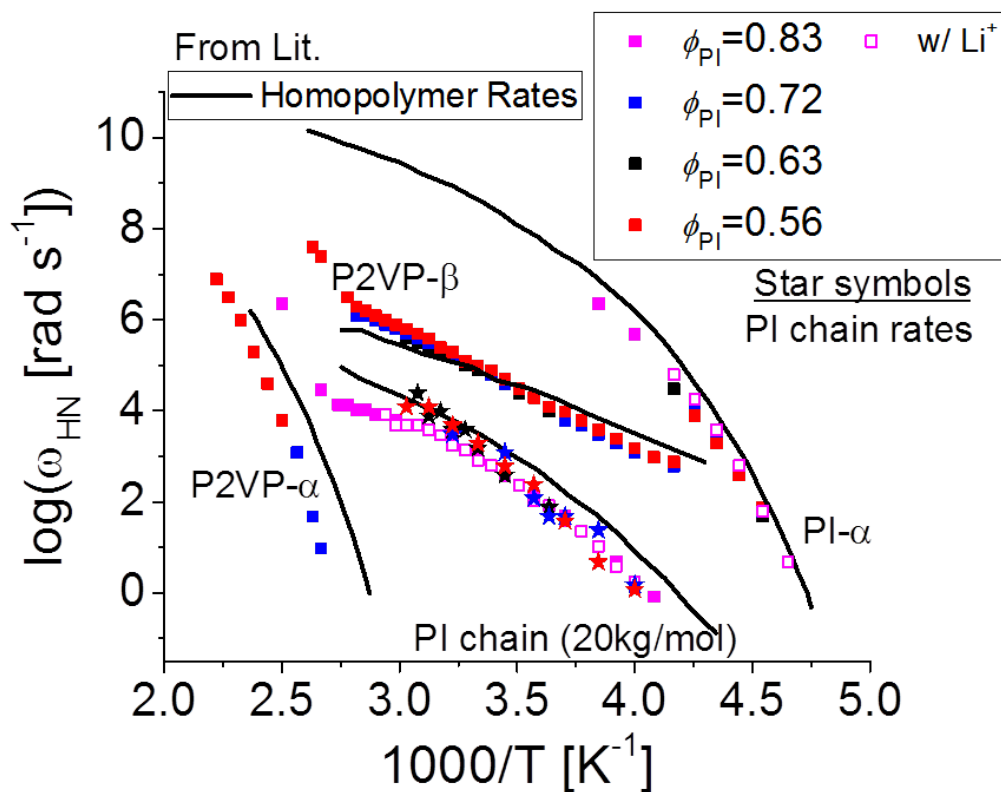


Figure 49: The relaxation rates for the PI and P2VP relaxations for the block copolymers as labeled on the plot. Homopolymer rates from the literature are shown as solid lines. The activation energy of the P2VP β relaxation is observed to deviate from that of the homopolymer.

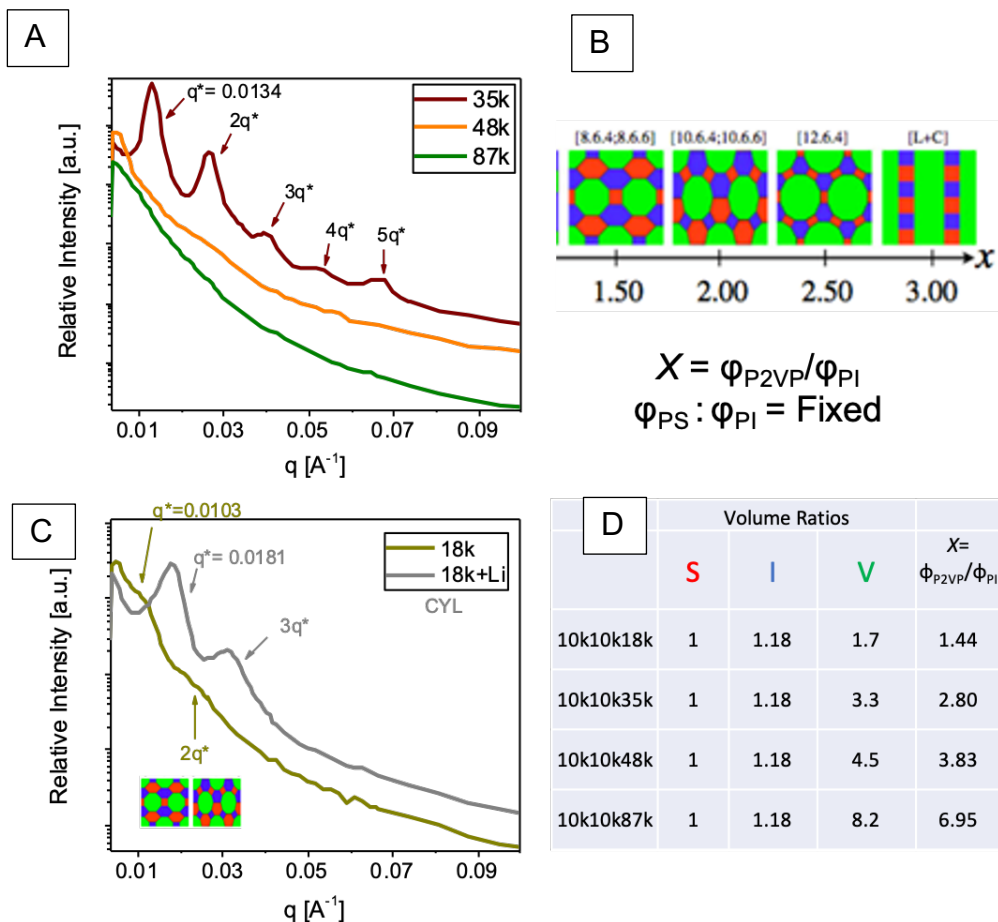


Figure 50: The SAXS profiles for the PSSIP2VP miktoarm star terpolymers with P2VP block molecular weights of 35kg/mol, 48kg/mol and 87kg/mol (A), and the simulated Archimedean tiling patterns from refs [227, 255] for different P2VP:PI volume fraction ratios (B). The SAXS profile for the miktoarm star terpolymer with 18kg/mol P2VP block with and without LiClO₄ (C), and the relative volume fraction ratios for the four terpolymers (D).

The dielectric spectra following salt doping for the 10k10k18k polymer (not shown) revealed the similar strong, low-frequency conductivity contribution that is observed in Figure 44A. Thus, the 10k10k35k polymer was the only neat system to produce well resolved phases and forms lamellar scattering peaks[256] in Figure 50A.

The dielectric spectrum of this 10k10k35k polymer is shown in Figures 51A and 51B for two selected temperatures where similar spectral characteristics are observed as for the PI-P2VP polymers. A HN function for the β -relaxation of the P2VP block is subtracted from the spectrum revealing asymmetric peaks at frequencies that are roughly characteristic of the PI α relaxation at different temperatures shown in Figure 51C. However, no clear chain relaxation is observed. This analysis was repeated for the other four polymers at $300\text{ K} \leq T \leq 220\text{ K}$, and the data for each system is normalized by the PI volume fraction and shifted along the frequency axis by the PS-PI master curve shift factors to reveal the pseudo-mastercurve spectra in Figure 52. Only the analysis of the dielectric spectra of the 10k10k48k miktoarm reveals peaks that are characteristic of the PI α and chain relaxations (see Fig. 52C).

In Figures 53A and 53B, the dielectric strength and HN α parameter ($\gamma = 1$), respectively, for the P2VP β -relaxation are plotted against temperature for the four PSPIP2VP and four PI-P2VP polymers. It can be seen that there is an increased $\Delta\epsilon_{\text{P2VP-}\beta}$ for the 20k10k diblock system and for the 10k10k87k and 10k10k35k miktoarm systems. This increased dielectric strength may be due to poor phase separation causing conformational changes in the P2VP chains as has been explained for tacticity changes [254]. However, this dielectric results is not reflected by the phase separation of the miktoarm systems in Figure 50 even with reproducible duplicate data. It is possible that annealing prior to dielectric measurements did not result in the same phase separation results as for the x-ray scattering samples.

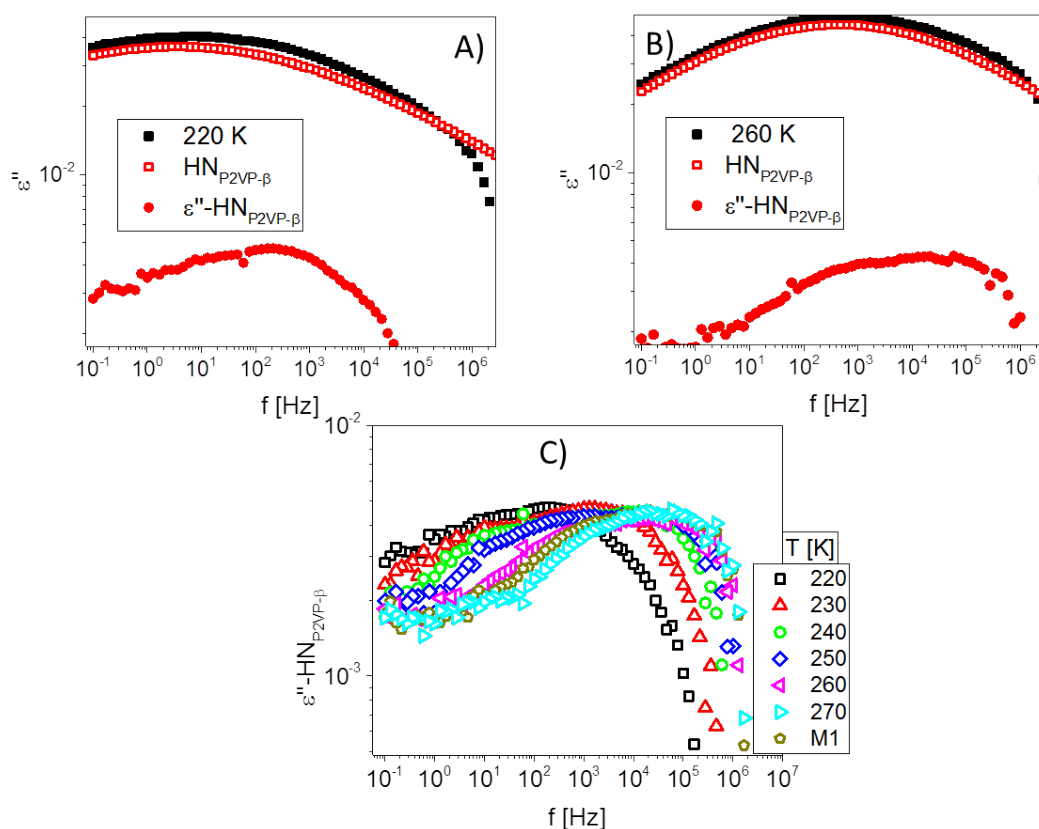


Figure 51: The dielectric spectrum of the PSPIP2VP miktoarm terpolymer with 35kg/mol P2VP block at $T = 220$ K (A) and $T = 260$ K (B). In (A) and (B), the solid black symbols are the dielectric loss, open red symbols are the HN functions for the P2VP β -relaxation and the red solid symbols are for the HN function subtracted from the loss spectra. In (C), the subtracted data is shown for multiple temperatures.

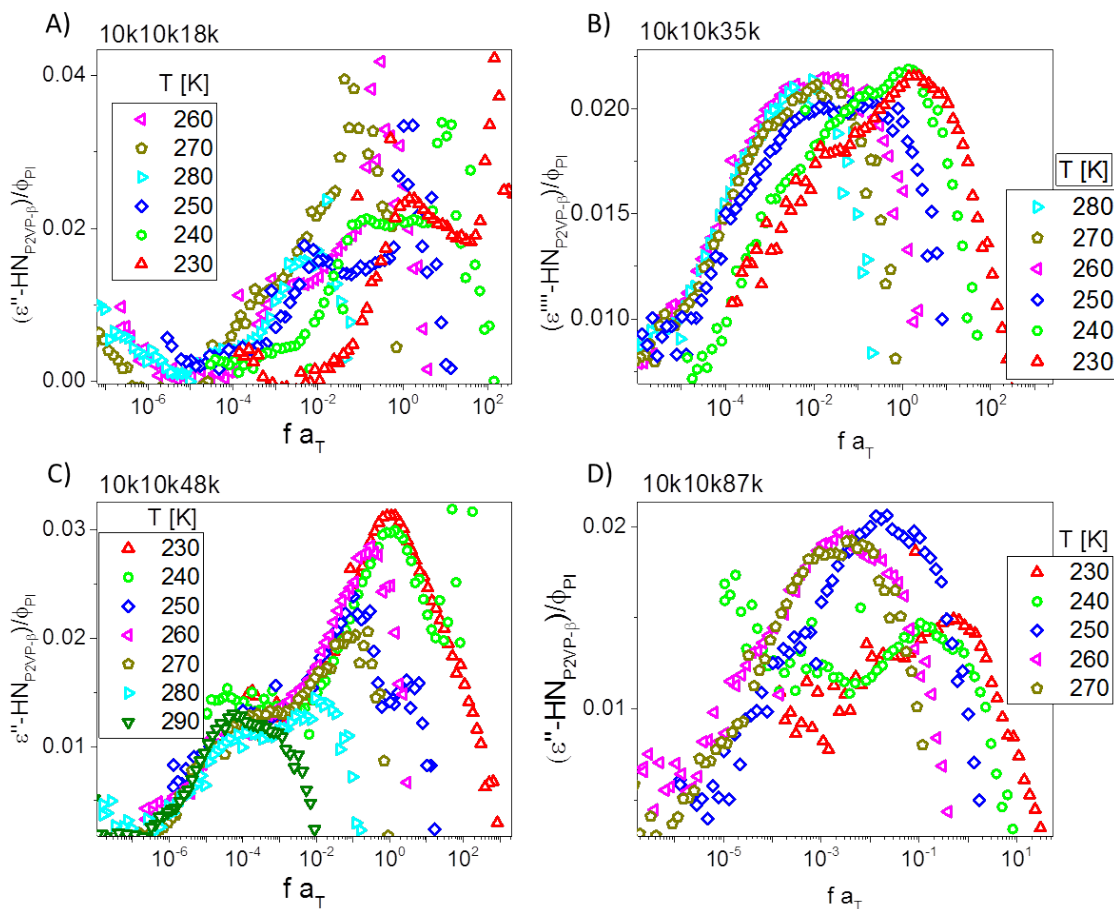


Figure 52: The pseudo-matercurves for the 10k10k18k miktoarm terpolymer (A), 10k10k35k miktoarm terpolymer (B), 10k10k48k miktoarm terpolymer (C), and 10k10k87k miktoarm terpolymer (D). These plots are produced by subtracting the HN function for the P2VP β -relaxation from the dielectric loss spectra at each temperature and normalizing the data by the ϕ_{PI} and shifting by a_T along the frequency axis.

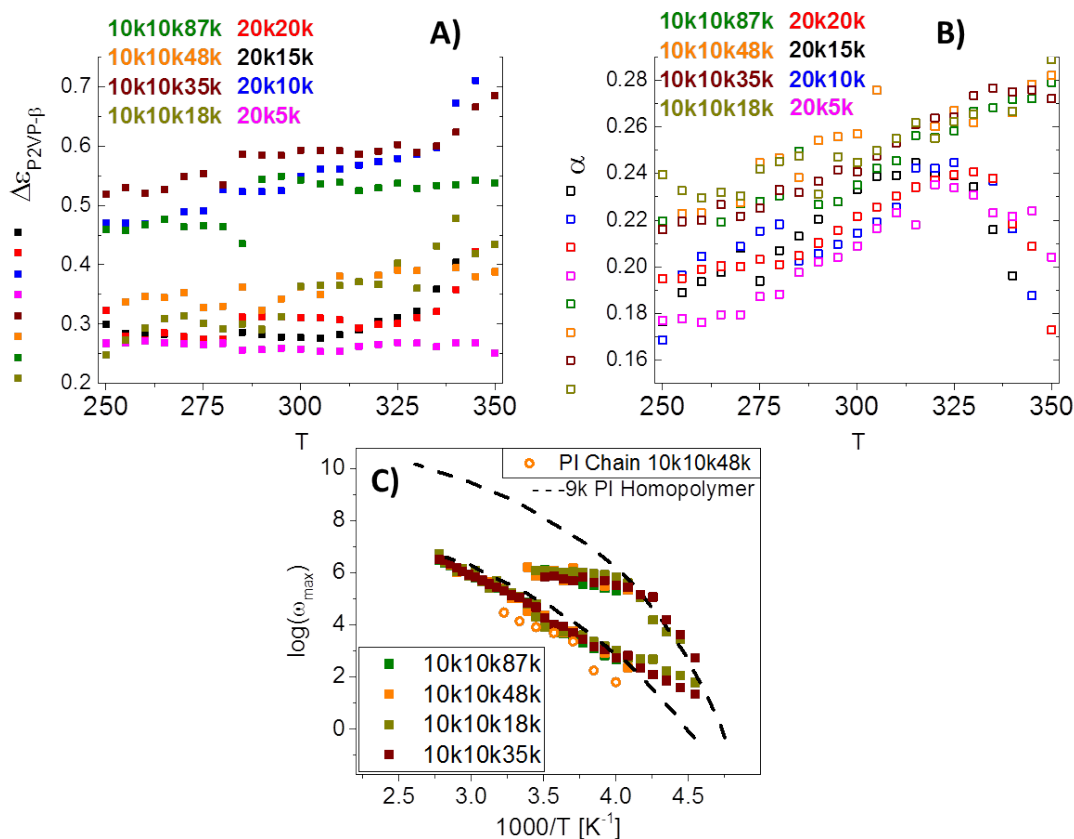


Figure 53: The dielectric strength of the P2VP β -relaxation HN functions $\Delta\epsilon_{P2VP-\beta}$ (A) and the α -parameter for the P2VP β -relaxation HN functions (B) used to subtract this relaxation from the dielectric loss spectra at each temperature. Also, the peak rates for the relaxation processes observed for the PSPIP2VP miktoarm star terpolymers (C). The colors for the data match the color of the polymer labeled in the figure.

The α parameter for the P2VP- β HN fits in Figure 53B reveal a narrowed peak for the miktoarm polymers compared to the linear diblock copolymers. This is likely due to the slower 20kg/mol PI chain relaxation in the diblock systems that contributes to the dielectric spectra at lower frequencies, whereas the 10kg/mol PI block chain relaxation in the miktoarm star terpolymers is expected to appear at almost the exact timescales as the P2VP β -relaxation.

The relatively low ϕ_{PI} for the miktoarm systems can be expected to result in reduced contributions to the dielectric spectrum from the PI chains and segments. Therefore, the primary relaxation measured for the miktoarm star terpolymers is the P2VP β process. As shown in Figure 53C, the chain relaxation for the 10kg/mol PI block is expected to be measured at almost the exact same temperatures and timescales as the P2VP- β relaxation [46]. This coincidence of the PI chain and P2VP- β polarizations makes the deconvolution of these relaxations much more difficult than for the 20kg/mol PI block in the linear PI-P2VP systems. This use of a 10kg/mol PI block may ultimately be an experimental design pitfall for this study.

Finally, the rates for the slower relaxation peak for the 10k10k48k miktoarm polymer revealed from the analysis in Figure 52C is shown in Figure 53C and exists at timescales and temperatures as expected for PI in other block copolymer systems (e.g. 4 times slower than for the homopolymer). It is possible that the PI chain relaxation timescales are altered for the other three miktoarm star terpolymers. Particularly, in Figure 53C, the rates of the PI α relaxation in the miktoarm systems has an unexpected deviation from the VFT temperature dependence at $\sim 240K$. This may be due to restricted dynamics of the PI block, but does not account for the PI chain relaxation only being observed for the 10k10k48k system. To conclude, while the measurement of the PI chain dynamics were not able to be reproduced from the measurements of all of the miktoarm terpolymers, the possibility for observing the PI chain relaxation is promising for future experiments.

Conclusions

This study examines the dielectric relaxations and block copolymer morphologies of PI-P2VP block copolymers using broadband dielectric spectroscopy and small angle x-ray scattering, and also investigates the relaxations in PSPI-P2VP miktoarm star terpolymers. The local dynamics of the P2VP block contribute a strong dielectric β -relaxation at similar timescales as the PI chain relaxation, and two methods to parse these relaxations were used to deconvolute these dynamics. First an experimental approach of solvating LiClO_4 into the P2VP block revealed that the β -relaxation contribution to the dielectric loss is suppressed and a faster relaxation of coordinated P2VP segments with the salt is observed. For the lower ϕ_{PI} systems, extremely strong contributions from long range ionic conductivity drown out other relaxations making this exponential approach limited to the system with discrete P2VP domains. Next, the analytical approach of fitting the data with the empirical HN function to directly subtract contributions to the ϵ'' from the P2VP β -relaxation was performed. This approach revealed the PI α and chain relaxations that were hidden beneath the strong β -relaxation for the linear PI-P2VP diblock systems with variable outcomes for the miktoarm star terpolymers. The HN fitting parameters for the PI relaxations in the PI-P2VP polymers were compared with the relaxation shapes of the PI dielectric normal modes in the literature for PS-PI systems. The fits for the PI in the PI-P2VP block copolymers were in agreement with the literature data which suggests that the PI chain relaxation is specifically dependent on the thermodynamics of phase separation and not the polarizations of the counter block for constant thermodynamic states of each block. This however, is not the case for the miktoarm star terpolymers where the PI chain relaxation was observed for only one system.

Chapter 5: Dielectric Relaxations of A_nB_m Miktoarm Star Copolymers: Lamellar Systems

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Kinsey, T., et al., *Impact of Molecular Architecture on Dynamics of Miktoarm Star Copolymers*. Macromolecules. 2018. **51**(14): p. 5401-5408.

The polymers in this chapter were synthesized by WW under guidance from KH using methods developed by KH and JM at the CNMS. All of the polymers were prepared for measurement and measured by TK in the laboratory of SMK, JS or at Duke SMiF with help from Justin Gladman. The manuscript was primarily written by TK with edits, comments and revisions from EUM, SMK and JS. WW, KH and JM were the primary writers for the synthesis part of the Materials and Methods section.

Abstract

Broadband dielectric spectroscopy (BDS) is used to probe the chain and segmental dynamics of A_2B_2 and AB_2 miktoarm star copolymers based on polystyrene (PS, A block) and polyisoprene (PI, B block) that display lamellar morphologies as determined using small-angle X-ray scattering (SAXS). While no changes in the distribution of PI segmental relaxation times are observed with variation of the molecular architecture, an unexpected increase in the normalized PI chain relaxation intensity is realized for AB_2 miktoarm star copolymers as well as a change in the distribution of chain relaxation rates as compared to A_2B_2 and AB diblock copolymer systems. This result is attributed to asymmetry in the molecular architecture near the junction point, which affects the osmotic constraint of the tethered PI chains within the interfacial region of the lamellae. The results

highlight the importance of macromolecular design on fundamental chain dynamics in phase separated thermoplastic elastomers.

Introduction

The ability to design block copolymers and tune their morphology adopted upon microphase separation makes them promising for many applications including drug delivery, lithography, filtration, super-elastomers and polymer networks for batteries, solar cells, fuel cells, actuators, field-effect transistors, and electrochromic devices.[257-260] With advances in anionic polymerization strategies, it is now possible to develop topologically complex polymer architectures and exert control over individual elements of morphology, including domain size and geometry, which can affect material properties at macroscopic length scales.[261, 262] For instance, miktoarm (mixed arm) star copolymers with chemically distinct arms connected at a central junction point (hetero-arm stars) provide access to unique phase separated structures that possess properties not observed in regular linear block copolymers.[209, 210, 212, 215, 261-264] Furthermore, asymmetric miktoarm architectures have been shown to adopt morphologies that are different from their linear counterparts, including smaller domain spacing with increasing number of arms.[216, 265-267] Recent experimental and computational studies reveal that mechanical properties, such as strength as well as percentage recovery after strain for asymmetric miktoarm star copolymers, are superior in comparison to linear systems.[215, 263, 268-270] The origin of these property enhancements presumably arises from changes in polymer dynamics at the interface between microphase-separated domains that are a consequence of changing the molecular architecture.[120, 210] While several studies report dynamical properties of linear diblock systems, there are only a few experimental studies focusing on fundamental dynamics of block copolymers having complex molecular architecture.[210, 212, 224, 271, 272] To our knowledge, there are no reports of systematic experimental studies on how

polymer dynamics are influenced by different architectures within the same morphology upon microphase separation.

To address this gap, broadband dielectric spectroscopy (BDS) is used to investigate the impact of molecular architecture on chain and segmental dynamics of (polyisoprene) (PI) in poly(styrene-isoprene) miktoarm star copolymers that form a lamellar morphology. Specifically, miktoarm stars of type A₂B₂ and AB₂, which contain two arms of PI and one PS arm, are studied and compared to linear AB diblock systems. The partial orientation of the non-inverted monomeric dipoles within the cis-1,4 PI backbone (i.e. Type-A polymer) results in a dipolar relaxation associated with chain end-to-end motion as probed using dielectric measurements.[49, 57, 89, 92, 126] This end-to-end dipole vector fluctuation corresponds to the normal mode relaxations of the polymer chains. Furthermore, dynamics associated with monomeric dipoles that are perpendicular to the polymer backbone in the Type-A polymer are also probed using dielectric spectroscopy. This relaxation is deemed the segmental- or α -relaxation and reflects the dynamic glass transition.[148, 158, 221] Analyses of the timescales and shapes of these dielectric relaxations give insight into the constraints on PI segment and chain motions due to local friction between segments, entanglement dynamics, phase separation, tethering of chain ends, etc.[125, 126, 136, 273, 274] The results presented in the current study show that no change in the shape of the PI α -relaxation is observed as the architecture is varied for lamellar forming systems. However, the AB₂ system displays an unexpected change in the distribution of PI chain modes along with increased relaxation intensity as compared to the A₂B₂ and diblock systems. These results highlight the influence of the simple nonlinear macromolecular architectures, specifically in the miktoarm star, on chain dynamics in phase separated systems.

Materials and Methods

Two different miktoarm star copolymers which both contain atactic-polystyrene and polyisoprene which has noninverted dipoles through synthetic control of high cis-1,4 microstructure. Specifically, a 4-miktoarm PS₂PI₂ star copolymer as well as a 3-miktoarm star PSPI₂ copolymer were synthesized by anionic polymerization in benzene with sec-butyl lithium as the initiator. The polymerizations were performed using all-glass reactors with break-seals under high vacuum, and a chlorosilane linking agent was used to generate the branched topology and microstructure, as previously reported.[262] Molecular weights were determined using size exclusion chromatography with light scattering and viscosity detectors. The key characteristics of the polymers are presented in Table 10.

The microphase separated morphology adopted by the copolymers was characterized using a Ganesha small angle X-ray scattering (SAXS) instrument. A Novocontrol High Resolution Alpha Dielectric Analyzer equipped with a Quatro Cryosystem was used to probe chain and segmental dynamics of the PI block. It is worth noting that the PS block of the 3-miktoarm sample is deuterated for future studies using neutron scattering, but the results obtained by BDS and SAXS techniques at the temperatures reported are not affected by this isotopic substitution. Samples for BDS and SAXS studies were prepared by hot pressing under N₂ atmosphere at 150 °C for at least 15 min. For BDS measurements, a film having a thickness of 100 μm film was sandwiched between two 10 mm diameter brass electrodes with 100 μm diameter glass silica rods as spacers. The films were thereafter thermally annealed in the spectrometer cryostat for more than 6 h at 430 K under N₂ to erase their thermal history, after which they were cooled to 290 K prior to measurement. The dielectric response was measured over the temperature range $220\text{ K} \leq T \leq 400\text{ K}$ in increments of 10 K in the frequency range spanning $10^{-1} \leq f \leq 10^6\text{ Hz}$.

Table 10: Characteristics of copolymers in Chapter 5.

Sample	$M_{w,PS}^a)$ (kg/mol)	$M_{w,PI}^a)$ (kg/mol)	$M_{w,total}$ (kg/mol)	M_w/M_n	ϕ_{PS}	$\epsilon_{Milner}^{b)}$	σ (nm ²) _{c)}
PS ₂ PI ₂	16.4	23.6	80.0	1.01	0.37	1.17	6.06
PSPI ₂	18.0	10.0	30.0	1.02	0.43	1.45	8.03
PSPI[119]	41.8	49.1	91.0	1.07	0.46	-	6.53 ^{d)}

^{a)}Molecular weight per arm

^{b)} $\epsilon=(n_a/n_b)(l_a/l_b)^{1/2}$

^{c)}Area per junction point within lamellae

^{d)}Domain spacing estimated to be 46 nm[275]

The dielectric data presented herein are restricted to temperatures below 360 K, that is, below the calorimetric glass transition temperature of the PS block ($T_{g,PS}$). This ensures the phase separated PS blocks remain glassy, which diminishes their direct contribution to the relaxation spectra and allows chain and segmental dynamics of the PI blocks to be studied. The samples for SAXS measurements were annealed for 6 h at 430 K under N_2 and then cooled to room temperature before measurement.

The area per junction point (σ) for each polymer used in this study was calculated using Eqn. 80, and the values are displayed in Table 10. The polyisoprene density (ρ_{PI}) is assumed to be constant and has a value of 0.856 g/cm³.^[266] The PI block molecular weight ($M_{w,PI}$) is the molecular weight of both arms added together for each polymer as described in the literature.^[267] The domain spacing (d) is calculated from the q^* peak measured by SAXS. Avogadro's number (N_a) is also used.

$$\sigma = \frac{2M_{w,PI}}{N_a \rho_{PI} (1 - \phi_{PI}) d} \quad 80$$

Data for σ of a linear diblock copolymer was taken from the literature and used to compare dielectric loss measurements to that our miktoarm samples.^[119] To calculate σ for the linear PS-*b*-PI polymer, a domain spacing was estimated from a PS-PI diblock copolymer having similar molecular weight. Hashimoto et. al. reported the domain spacing for a 49.5k PS-*b*-47.5k PI sample measured by electron microscopy to be $d=46$ nm.^[275] Therefore, 46 nm was used for the domain spacing of the 42k PS-*b*-49k PI diblock copolymer from which the dielectric data is used. The higher molecular weight of the polymer used to estimate d results in an overestimation of the area per junction of the linear diblock for which the dielectric data is used. Therefore, the linear diblock would still display a comparable area per junction as the 4-miktoarm system. We contend that this estimation allows for a reasonable calculation of σ for the linear diblock system.

Finally, a transmission electron micrograph (TEM) image of the PS₂PI₂ sample is included here (see Fig. 54) to provide insight into the importance of cross-correlation of the orientation of chain end-to-end dipole vectors due to alignment of lamellae. The 100 nm sample for TEM was cryo-ultramicrotomed at -90°C after measurement by BDS. The sample was collected onto a 400 mesh copper TEM grid and stained with OsO₄ vapor (using a 4 wt% aqueous solution) for 3 hours. The sample was imaged using a Zeiss Libra 120 TEM (at the Oak Ridge National Laboratory, accessed through the CNMS User Program (proposal CNMS2017-418)).

Results and Discussion

The molecular weights of the miktoarm polymers studied were chosen by applying Milner's theory which predicts the morphology of hetero-arm star copolymers to ensure that they form lamellar domains upon microphase separation (see the Introduction to Part I).[276] The locations on the Milner diagram for the two polymers in this chapter can be found in Figure 55. Some studies have shown that morphology is not accurately predicted for miktoarm polymers that fall close to the boundaries of the Milner phase diagram.[104, 266, 277] Therefore, the actual morphologies must be measured. SAXS was used to confirm lamellar morphology for both the PSPI₂ and PS₂PI₂ polymers, and to determine the domain spacing, d , of the lamellae in each sample from the first Bragg peak, q^* , using the relation $d=2\pi/q^*$, see Figure 56.

Maintaining lamellar morphology among samples allows the effect of architecture on the dielectric response of these materials to be isolated from changes in morphology. A broadened $2q^*$ peak is observed in Figure 56 for the 3-miktoarm polymer suggesting a lower degree of long-range lamellar ordering.

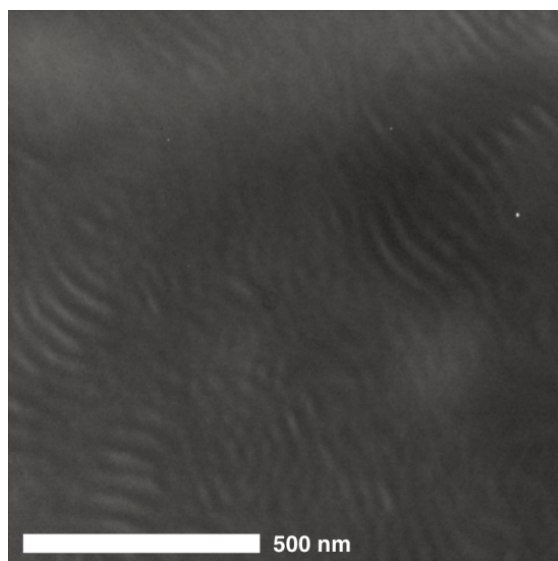


Figure 54: TEM image of microtomed PS₂PI₂ sample showing lamellae orientation that is consistent with relative alignment parallel with the electrode surfaces. With respect to the image the electrodes would be relatively aligned on the right and left sides.

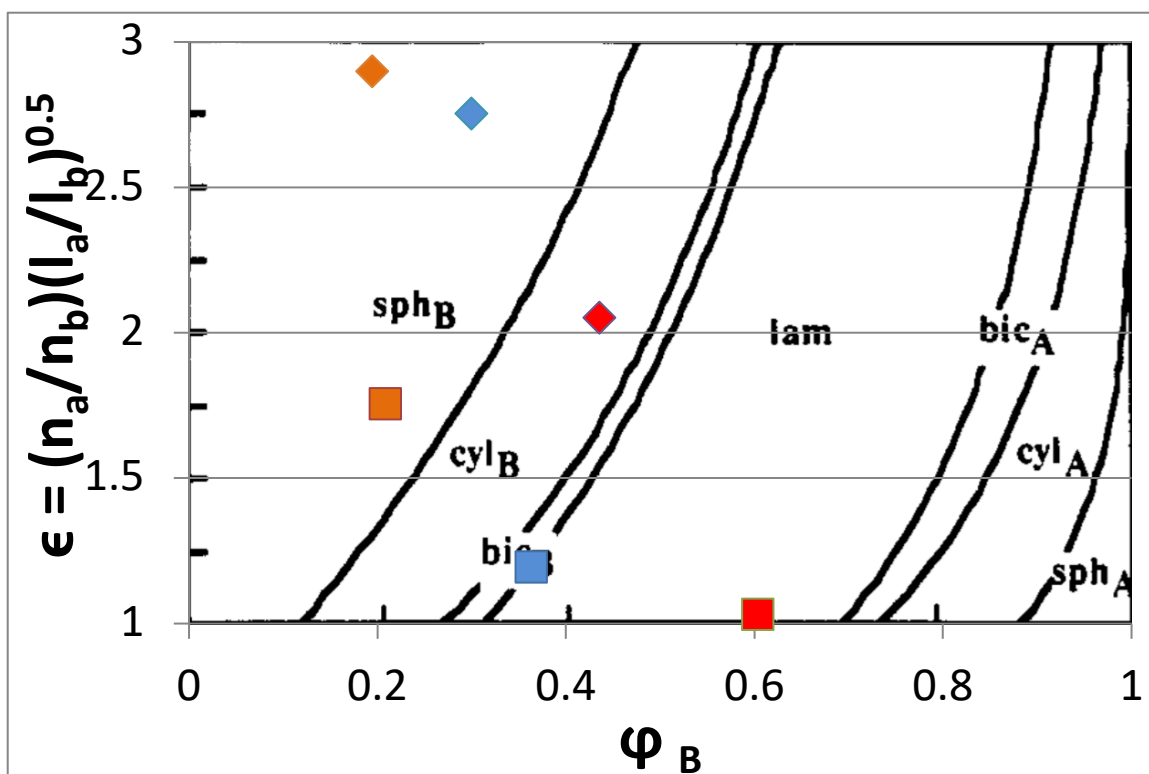


Figure 55: Milner diagram for the PS₂PI₂ (squares) and PSPI₂ (diamonds) miktoarm star copolymers in Part I Chs. 4 and 5. The symbols follow from orange to blue to red for low to high PI molecular weight. (16k₂9k₂: orange square; 16k₂24k₂: blue square; 16k₂52k₂: red square; 18k₁₀k₂: red diamond; 18k₁₈k₂: blue diamond; 18k₃₂k₂: orange diamond)

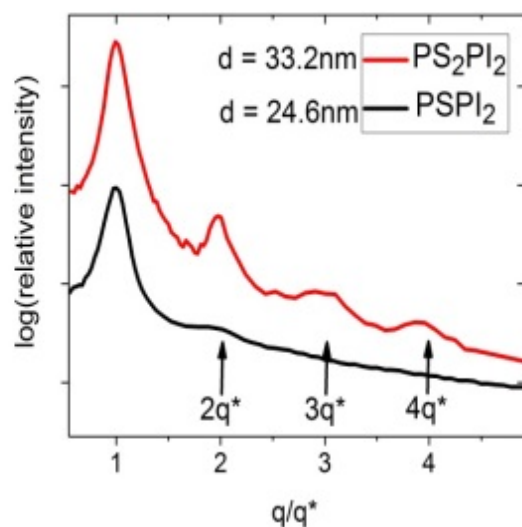


Figure 56: Small-angle x-ray scattering profiles of PS₂PI₂ and PSPI₂ miktoarm star copolymers display patterns of behavior consistent with lamellar morphology. Long-range order is observed in A₂B₂, while the broadened 2q* peak in AB₂ architecture is indicative of a lower degree of long range order.

It is plausible to assign the decreased ordering in the 3-miktoarm lamellae to the fewer number of PS arms rather than to a decrease in $M_{w,PI}$ because of an observed increase in the Flory interaction parameter, χ , with increasing number of arms for miktoarm copolymers.[216] The interfacial area per junction point, σ , was also calculated for the miktoarm copolymers based on the values in Table 10 and as discussed in the Materials and Methods section above. The increase in σ for the PSPI₂ system relative to polymers with architecturally symmetric block is consistent with previous findings.[267] These results are also discussed later in terms of their possible effects on PI chain dynamics.

The dielectric loss (ϵ'') spectra at three temperatures, which were measured by BDS for the miktoarm copolymer systems, are plotted in Figure 57. They display peaks associated with energy dissipated through dipolar relaxations under an applied frequency-dependent electric field ($10^{-1} \leq f \leq 10^6$ Hz) at different temperatures. The spectra reveal dynamics of dipolar moieties within the polymers at specific timescales.²⁷ The dielectric loss relaxations are related to the corresponding time dependent dielectric relaxation function, $\Phi(t)$, by:

$$\epsilon''(f) = -\Delta\epsilon \int_0^\infty \frac{d\Phi(t)}{dt} \sin 2\pi f t dt \quad 81$$

where f is the frequency of the electric field (in Hz) and $\Delta\epsilon$ is the dielectric strength of the relaxation. Poly(styrene-*block*-isoprene) copolymers (PSPI) at $T < T_{g,PS}$ display a fast, lower-temperature ($220 \leq T \text{ (K)} \leq 260$) peak associated with PI block segmental dynamics (α -relaxation), as well as a slow, higher-temperature process corresponding to the chain relaxation of PI (normal mode motion) that is dependent on molecular weight.

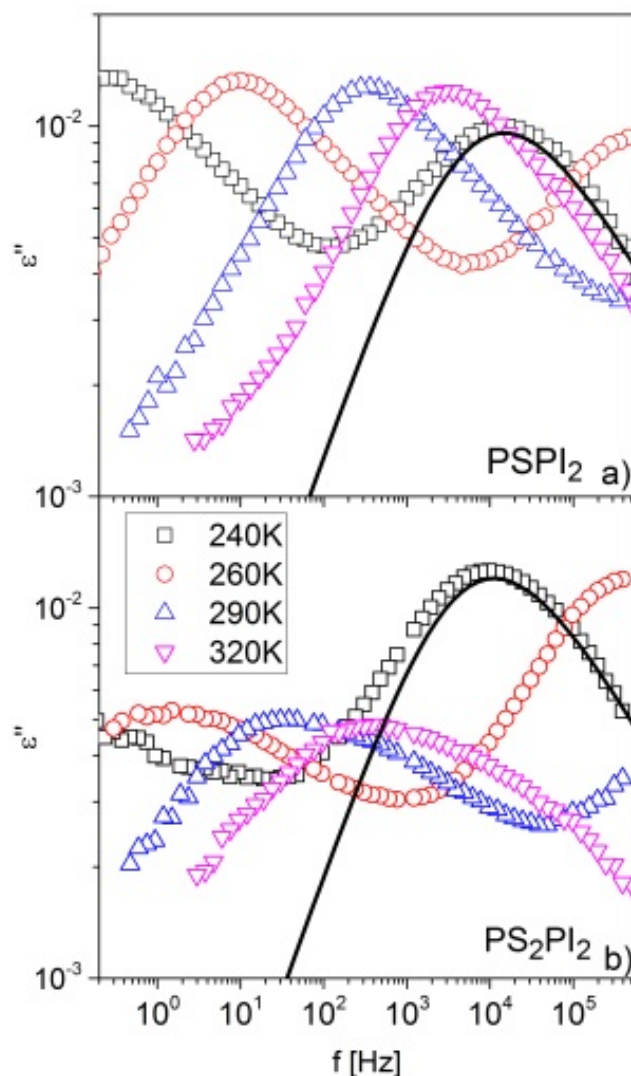


Figure 57: Isothermal dielectric loss spectra of (a) PSPI2 miktoarm stars and (b) PS₂PI2 miktoarm stars at various temperatures. At any given temperature, peaks corresponding to the segmental and chain relaxation processes appear at high and low frequency, respectively. HN fits for the segmental relaxation at 240K are displayed as solid lines. See Supporting Information for fit parameters.

The slower PI chain relaxation arises due to a portion of monomeric dipole vectors aligned parallel to the polymer backbone (type-A polymer).[89] At $T < T_{g,PS}$, no direct contribution from the PS segmental dipoles are observed. Due to characteristics of the dipolar alignment in the Type-A polymer, the autocorrelation function of the polarization, $\mathbf{P}(t)$, is related to the parallel ($\mu^{\parallel}$) and perpendicular ($\mu^{\perp}$) portions of the dipole moments in the material and is also related to $\Phi(t)$. If the fast and slow processes are well separated in the time domain, then they can be expressed as a sum of independent relaxations through:

$$\frac{\langle \mathbf{P}(t) \cdot \mathbf{P}(0) \rangle}{\langle [\mathbf{P}(0)]^2 \rangle} = \frac{\sum_j \sum_m \langle \mu_{ij}^{\parallel}(t) \cdot \mu_{im}^{\parallel}(0) \rangle + \sum_j \sum_m \langle \mu_{ij}^{\perp}(t) \cdot \mu_{im}^{\perp}(0) \rangle}{\sum_j \sum_m \langle [\mu_{ij}^{\parallel}(0)]^2 \rangle + \sum_j \sum_m \langle [\mu_{ij}^{\perp}(0)]^2 \rangle} = \Phi(t) \quad 82$$

where $\langle - - \rangle$ denotes the equilibrium ensemble average. In Equation 5.3 we have ignored cross terms of $\mu^{\parallel}$ and $\mu^{\perp}$ because it has been shown that dipole-dipole interaction energies of neighboring PI segments within a single chain are small relative to the thermal energy of these dipolar motions.[278, 279] Thus, if we sum the portion of parallel dipoles in the dielectric relaxation function we can calculate the autocorrelation function of the end-to-end vector fluctuation, $\mathbf{R}_i(t)$, of a Type-A polymer using:

$$\frac{\sum_j \sum_m \langle \mu_{ij}^{\parallel}(t) \cdot \mu_{im}^{\parallel}(0) \rangle}{\sum_j \sum_m \langle [\mu_{ij}^{\parallel}(0)]^2 \rangle} = \frac{\langle \mathbf{R}_i(t) \cdot \mathbf{R}_i(0) \rangle}{\langle [\mathbf{R}_i(0)]^2 \rangle} \quad 83$$

Using Eqns. 81-83 the dielectric loss spectra of the three systems under investigation can be analyzed to monitor changes in relaxation dynamics of the tethered PI chains as a function of copolymer architecture.

In addition, there is a possibility of cross-correlation of polarized dipoles in PI chains in different polymers, $\sum_j \sum_{k \neq i} \langle \mu_i(t) \cdot \mu_k(0) \rangle$, will contribute to $\Phi(t)$ and as a result, this contribution must also be considered. It is worth noting that the

Reptation model assumes that this cross-correlation is negligible due to the fixed branch point in homopolymer stars [280]. In these miktoarm systems, the branch points are also fixed within the lamellar interface due to the glassy PS blocks. Furthermore, sample annealing in this study was performed in such a way to preferentially orient lamellae parallel to the electrodes. The TEM image of annealed 4-miktoarm star sample in Figure 54 confirms that the lamellae are oriented in such a way. It has been shown that the chain relaxation measured by dielectric spectroscopy for linear PSPI systems forming lamellae parallel to the electrode surfaces corresponds to modes of individual PI blocks. Therefore, with these facts in mind, it is reasonable to discuss the dielectric relaxations in these systems with the assumption that the effects of cross-correlation of dipoles among PI chains within differing polymers are negligible.

The dielectric loss spectra of each miktoarm polymer were first analyzed using frequency-temperature-superposition (FTS). This was done by shifting the dielectric loss spectra at each temperature ($220\text{K} \leq T \leq 320\text{K}$) along the frequency axis by a temperature dependent shift factor (aT) using a reference temperature of 270K. As seen in left panel of Figure 58 the temperature dependence of aT for the miktoarm star polymers are similar to those reported by Yao et. al. for lamellar PS-*b*-PI systems at a reference temperature of 273K.^[61, 92] The FTS representations (right panel of Fig. 58) of the dielectric loss spectra display peaks that superpose well up to 320K for the miktoarm samples suggesting the distribution of PI segment and chain relaxation times are temperature independent when full phase separation is achieved. (i.e., The shapes of the segmental and chain relaxations are temperature independent within the studied temperature range.) This is consistent with PS-*b*-PI data described in the literature and suggests that the PI segments and chains are interacting only with other PI segments and chains, and have local interactions similar to the homopolymer.^[46, 92, 119]

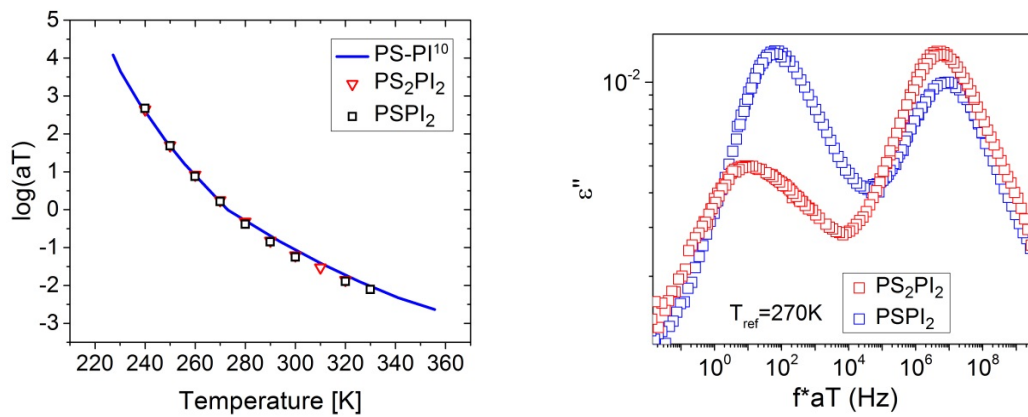


Figure 58: The temperature dependent shift factors, aT , used to apply the FTS shift to the dielectric loss data (left). The resulting master curves for the lamellae forming PS₂PI₂ and PSPI₂ polymers at 270K reference temperature (left). These aT values are compared to the shift factors from the literature for linear PS-PI block copolymers at a reference temperature of 273K.

To analyze the shapes of the dielectric loss spectra, the segmental relaxations at high frequencies in the FTS representation for all three polymers were fit using the Havriliak-Negami (HN) function in Eqn. 84 with parameters published by Jenczyk et. al. for lamellar forming PS-*b*-PI ($\alpha=0.65$ and $\beta=0.6$).[119]

$$\epsilon^*(\omega) = \Delta\epsilon_{HN} [1 + (i\omega\tau_{HN})^\alpha]^{-\beta} \quad 84$$

Because the FTS plots are only representative of the 270K spectrum, the frequencies of maximum loss f_n (which are related to the characteristic relaxation time τ_{HN} in Eqn. 81) and the dielectric strength of the relaxations, $\Delta\epsilon$ are arbitrary in this representation, but will be discussed later at each temperature. Following the fitting the segmental relaxations of the FTS data with Eqn. 84, the segmental relaxation was subtracted directly from the spectra. Because the HN is merely an empirical fitting function, subtractions of the segmental relaxation were completed such that a cut-off on the high-frequency wing of the chain relaxation decays with $\epsilon'' \sim f^{-1}$ as $f \rightarrow f_{\alpha, \max}$. This is done because of the assumption that cross-correlations of $\mu^{\parallel}$ and $\mu^{\perp}$ in Eqn. 82 cancel out, and therefore, the normal mode must show a cutoff as it approaches the rate of maximum loss for the α -relaxation in accordance with the Rouse model.[46] This cut off was chosen to be Debye-like and at such low intensities at overlapping frequencies, the shape of the chain relaxation is not affected by subtraction of the HN fit to the α -relaxation.[281] This analysis holds as long as the assumption that cross-correlations of the sub-chain dipoles are canceled at high frequencies due to low dipole-dipole interaction energies is maintained. This cutoff is observed after subtraction of the segmental relaxation in Figure 59. Finally, a second HN function was fit to the normal mode for each polymer to describe the remainder of the FTS spectrum with shape parameters shown in Table 11.

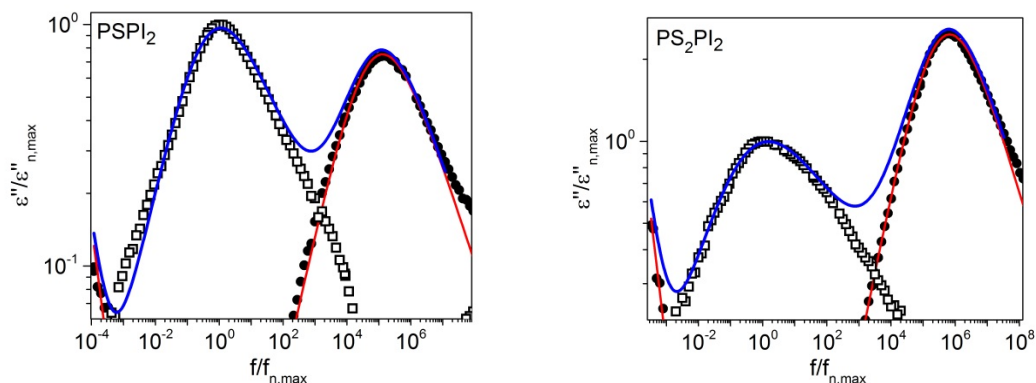


Figure 59: Dielectric loss spectra from FTS for PSPI₂ (left) and PS₂PI₂ (right) used to fit segmental and chain relaxations. Blue line: Two HN fit functions to segmental and chain relaxations with conductivity contribution added at low frequencies. Red line: segmental HN and conductivity fits. Open black squares: FTS data with segmental HN and conductivity subtracted revealing chain relaxation. Closed black circles: FTS data with chain HN subtracted revealing segmental relaxation. (Note: These data have been normalized by chain relaxation peak frequency; therefore, only the shape parameters are relevant.)

Table 11: HN fitting parameters for PI chain relaxations in lamellae forming miktoarm copolymers

Sample	α	β
PS ₂ PI ₂	0.58	0.26
PSPI ₂	0.54	0.80

The spectral shape associated with the segmental relaxations for these polymers are shown in Figure 60, as revealed through the subtraction from the HN fits to the chain relaxation, is unchanged for all architectures probed. This confirms that the distribution of the segmental relaxation times for PI segments is architecture-independent for the lamellar morphology.[138, 271, 272] This is consistent with the expectation that the dielectric loss associated with segmental relaxation corresponds to fluctuations at the length-scale of 2-3 nm.[91] Moreover, this relaxation governs the PI glass transition and, therefore, is not likely to be affected by tethering of chains to a planar glassy interface or by changing the architecture, as long as good phase separation is achieved and the polymers do not crystallize.[282]

Using the fitting parameters from the FTS analyses, two HN functions are added together to describe the dielectric loss data confidently at each temperature. Using Eqn. 85 below and HN fit parameters at each temperature for these two polymers the rates of maximum loss ($\omega_{\alpha, \max}$ or $\omega_{n, \max}$) for corresponding α or chain relaxations are determined, respectively.

$$\omega_{\max} = 2\pi T_{HN}^{-1} [\sin(\pi\gamma/2(\alpha+1)) / \sin(\pi\gamma\alpha/2(\alpha+1))]^{-\gamma} \quad 85$$

The $\omega_{\max}$ data are displayed in the activation plot in Figure 61 along with α -relaxation rates for a PI homopolymer and for a lamellar-forming PSPI linear block copolymer, which were extracted from literature.[46, 119] The solid lines in Figure 61 are fits to the $\omega_{n, \max}$ data using the Vogel-Fulcher-Tammann (VFT) equation which quantifies these temperature dependencies

$$\omega_{\max} = \omega_{\infty} \exp[B/T-T_0] \quad 86$$

where ω_{∞} is a characteristic rate, T_0 is the Vogel temperature and B is a parameter specific to the material. These parameters from the fitting the relaxation rates are found in Table 12.

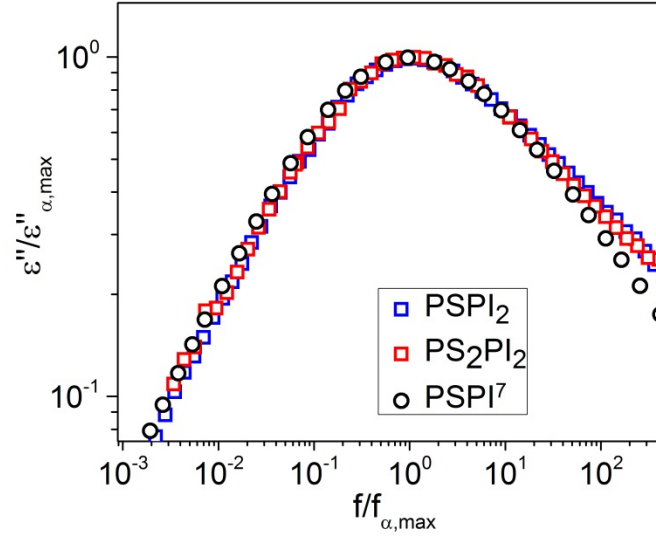


Figure 60: Dielectric loss segmental relaxation. The shapes of the revealed segmental relaxations are independent of architecture.

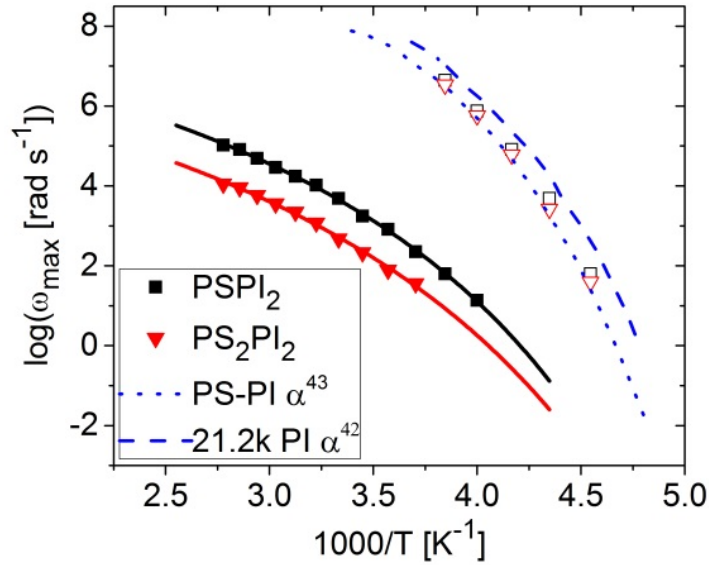


Figure 61: Temperature dependence of the $\omega_{n,max}$ (open symbols) and $\omega_{\alpha,max}$ (closed symbols) for miktoarm systems are displayed here. VFT fits ($\omega_{max} = \omega_0 \exp[B/(T-T_0)]$) are displayed as solid lines for peak chain relaxation rates. Also displayed are α -relaxation rates for a PI homopolymer (dashed line) and PSPI diblock copolymer (dotted line) taken from data in the literature.[46, 119]

Table 12: VFT parameters for temperature dependent PI chain relaxation rates for lamellae forming miktoarm star copolymers

	PS ₂ PI ₂	PSPI ₂
ω_{∞}	3.83×10^7	2.61×10^8
B	1668.1	1573.6
T₀	151.1	156.5

In comparison to the PI homopolymer, the $\omega_{\alpha,\max}$ in Figure 61 are slightly slower for all copolymer architectures, with the diblock system being the slowest, followed by the PS_2PI_2 , and the PSPI_2 . The frequency of maximum dielectric loss ($\omega_{n,\max}$) associated with the chain relaxation for PS_2PI_2 is roughly two times slower than $\omega_{n,\max}$ for PSPI_2 . This is reasonable since $M_{w,\text{PI}}$ in PS_2PI_2 is almost twice that of PSPI_2 . However, due to the tethering effect of the phase separated lamellar organization of the PI block to a glassy PS block, it is naïve to expect $\omega_{n,\max}$ to be comparable to the timescale of the *complete* reorientation of the chain such as in the homopolymer, and $\omega_{n,\max}$ must then correspond to end-to-end vector fluctuations of chains that relax similarly to the applied electric field. In several publications, Yao et. al. offer skepticism in comparing the chain relaxation peak times ($\tau_n = \omega_{n,\max}^{-1}$) among polymers that display different chain relaxation shapes.[283, 284]

To observe changes in the distributions of the chain relaxations and relative dielectric strengths ($\Delta\epsilon_n$) with architecture, the intensities of the slower chain relaxations (including data from literature[46, 119]) were divided by the PI volume fraction (ϕ_{PI}) to normalize by the fraction of chains contributing to the dielectric loss spectra within the volume of material being measured. As seen in Figure 62, after transforming the data in this way, broadening toward both high and low frequencies is observed for the chain relaxation of the miktoarm stars compared to that of the PI homopolymer. This broadened PI chain relaxation has been reported many times for linear PSPI and homopolymers confined at the mesoscale level, and it is attributed to the effect of thermodynamic confinement of chains causing them to move cooperatively in order to maintain constant segment density.[92, 119, 125, 126, 133, 136, 203, 285] Close inspection of the chain relaxation spectra for the PS_2PI_2 polymer (see Fig. 62) reveals a very similar shape to that of the PSPI diblock, with the former displaying slight broadening toward high frequencies. The similarity in the peak shape suggests that the effects of confinement of the chains in these two architectures are similar.

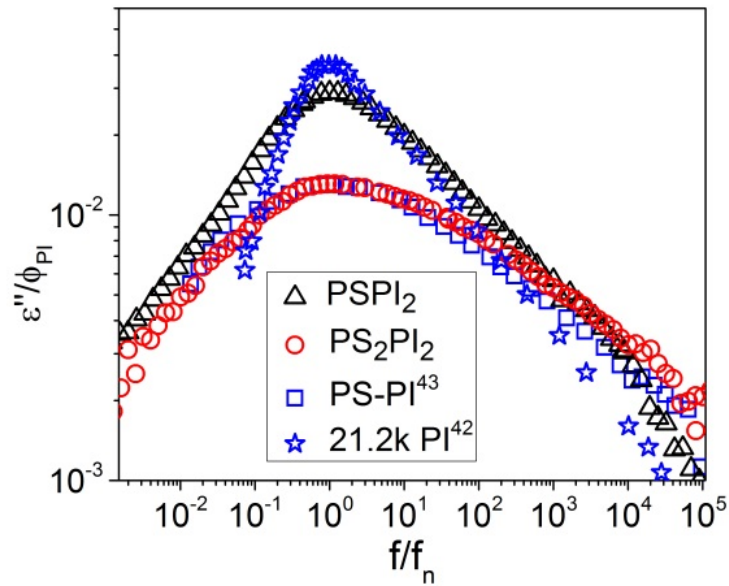


Figure 62: The dielectric loss spectra for the chain relaxation from FTS analysis has been normalized with respect to peak frequency and PI volume fraction for samples of various molecular architectures that adopt a lamellar morphology as well as a PI homopolymer (blue stars). Similar breadth of the chain relaxation is seen for block copolymer systems with an increased normal mode intensity for PSPI2 (black triangles) as compared to symmetric architectures, PS2PI2 (red circles) and PSPI (blue squares). Data from literature are colored blue. [46, 119]

At first glance, it may seem reasonable to attribute the slight changes seen in the shape of PS₂PI₂ and PSPI chain relaxations at high frequencies to differences in the $M_{w,PI}$. However, entanglement dynamics, which are enhanced with increasing molecular weight in homopolymers, have been shown to play a minimal role in block copolymer chain dynamics.[92] Also, for PI homopolymer stars, the chain relaxation is observed to broaden toward high frequencies with increasing number of arms and molecular weight, but only for molecular weights above the entanglement molecular weight.[203, 286] Here, the *higher* $M_{w,PI}$ in the diblock sample displays a *narrower* high frequency wing than the lower $M_{w,PI}$ in the PS₂PI₂ system. This is opposite of what one might expect in terms of broadening due to $M_{w,PI}$.

Previous studies of nanoparticle surface-tethered linear-PI as well as PI-stars have indicated that chains closest to the junction/tethering point are stretched due to crowding.[273, 274, 286-288] Molecular dynamics simulations have revealed that the chain relaxations perpendicular and close to the interface speed up with increasing phase separation (increase in χN) for diblock systems and we assume a similar effect in block copolymer systems with complex architecture.^[93, 274] We also expect the PI chains of the PS₂PI₂ to display this stretched conformation away from the interface and an increase in faster normal modes contributing to its dielectric chain relaxation. Furthermore, the dielectric strength ($\Delta\epsilon_n$) for the diblock and PS₂PI₂ star are essentially the same. This suggests that the dielectric loss correlates to the same PI chain motion in both the PS₂PI₂ as the PSPI diblock and that the cancelation of cross terms in $\Phi(t)$ for the PS₂PI₂ architecture is a plausible assumption. Therefore, the slightly broader chain relaxation peak of the 4-arm system relative to the diblock is attributed to an increase in the proportion of faster normal modes resulting from chains having to stretch away from the interface due to crowding. However, a dramatic change in the $\Delta\epsilon_n$ is observed when comparing the chain relaxation in the symmetric architectures to the PSPI₂ chain relaxation. There is a single report in the literature

describing changes in PI chain dynamics in a PSPI₂ compared to diblock and 3-miktoarm terpolymer architectures, but the effect of architecture was not decoupled from changes in morphology for the samples presented, which we describe here in terms of both $\Delta\epsilon_n$ and the $\Phi(t)$. [272]

The $\Delta\epsilon_n$ for the normal mode relaxation has been shown to be:

$$\Delta\epsilon_n = \frac{4\pi N_a \mu_{||}^2}{3k_B T M_{w,PI}} F \phi_{PI} \langle R^2 \rangle \quad 87$$

where N_a is Avogadro's number, $\mu_{||}$ is the monomeric dipole moment parallel to the polymer contour, k_B is Boltzmann's constant, and T is the absolute temperature. [49, 280] Here, F denotes the Kirkwood parameter which is assumed to be approximately unity. In order to compare relative dielectric intensities and shapes by normalizing by ϕ_{PI} (Fig. 62), we must assume that the change in the end-to-end distance and $M_{w,PI}$ are constant across all architectures. This assumption has been shown to be valid for PI homopolymers (where $\phi_{PI} = 1$), and invoked across studies of systems containing tethered PI chains and block copolymers containing PI. [134, 273, 274] If the change in architecture causes chain stretching such that some segments near the interface are immobilized, it is possible that normalization of the chain relaxation by ϕ_{PI} is invalid. Furthermore, if and $M_{w,PI}$ were to not scale due to immobilized segments, we would expect to observe this effect in the dielectric spectra as functionality of the junction point increases. However, this is not observed in our studies. The $\Delta\epsilon_n$ is effectively higher for the PSPI₂ system, which has a decreased junction point functionality compared to the PS₂PI₂ system and an increased junction point functionality compared to the PSPI system. Also, increasing functionality at the junction point and lowering molecular weight from the PSPI to the PS₂PI₂ showed no change in $\Delta\epsilon_n$ and very little change in the distribution of chain relaxation times. Therefore, we can continue to assume the dielectric relaxation strength is not likely to be the overarching cause for the change in the chain relaxation shapes with molecular

architecture, and we predict that M_{PI} and will scale similarly among similar architectures. A more exhaustive discussion of these conjectures will be discussed in Chapter 6.

While we have argued that cross-correlations from different chains in general may be neglected, but we would like to analyze a more specific possibility of cross-correlations of polarized dipoles between PI chains within the same macromolecule (due to connection at a common junction point). However, we believe this important consideration does not address the increase in the normal mode for the PSPI₂ system. To argue this, we discuss a hypothetical case where there is an increased density of chains near the junction point due to excluded volume. Several groups have made conjectures about decreased chain mobility due to excluded volume of polymers of complex architecture with a common junction point, as well as excluded volume effects in nanoparticle/polymer blends.[266, 267, 289, 290] It has been determined that an increase in isothermal osmotic compressibility correlates with increased excluded volume.[291] The increase in excluded volume of polymer chains near the junction causes anisotropy in the conformational entropy along the chain contour. Also, the increase in osmotic compressibility near the junction point may increase the dipole-dipole interaction potentials at the same time as the decrease in conformational entropy decreases the energy of thermal motion for the segments near the junction point. This would present a problem in accepting the assumption that cross terms in Eqn. 82 are canceled for *both* of the miktoarm systems. However, no evidence of such an effect is observed in the $\Phi(t)$ for the PS₂PI₂ normal mode, and it remains that the PS₂PI₂ chain relaxation shape is similar to that of the PSPI spectrum. Therefore, we continue to make the assumption that no dipolar cross-correlation is occurring at any point along the chain contour in the miktoarm systems.

Next, in comparing the breadths of the chain relaxations of all block copolymer architectures, it is observed that they are all very similar. However, the dynamics of the asymmetric PSPI₂ architecture shows an increase in the normal

mode intensity, almost matching that of the PI homopolymer. Block copolymers of different molecular weights that display similar morphologies are generally expected to have comparable breadths in the distribution of chain relaxation rates.[92, 125, 134, 272] Also, an increase in the number of arms at the junction point is expected to correlate with enhanced confinement on the PI chains due to stronger phase separation.[273, 292] Furthermore, because we assume cross-correlation of dipole polarizations to be canceled, it is reasonable that the changes in the normal mode intensity are simply due to changes in thermodynamic constraints of the chain motion for the PSPI₂ within the lamellae due to architecture. However, it would be appropriate to also consider a possibility of *motional* cross-correlation in chains of the same polymer near the junction point in the PSPI₂ polymer as explained below.

Elastic forces of two PI chains on the one PS chain may allow for cross-correlations of one chain end-to-end fluctuation, $\mathbf{R}_i(t)$, with that of neighboring chain tethered at the same junction, $\mathbf{R}_j(t)$ (where $i \neq j$), contributing an additional cross term to the chain autocorrelation or dielectric function in Eqn. 83.[278] The architectural asymmetry in the PSPI₂ system may cause subtle normal mode fluctuations of one arm to transfer through the junction point to the other arm effectively enhancing the mobility of the chains while maintaining constraints due to phase separation. In turn, this causes an additional contribution to $\Phi(t)$, which increase the intensity of the relaxation and changes the spectral shape of the dielectric loss peak. The argument for this effect is strengthened with the calculation of increased area per junction point, σ , for the PSPI₂ system, which is presented in Table 10. The decrease in conformational entropy near the junction would be counteracted by the energy involved in elastic forces on the junction point, subsequently increasing the motion of chains and, as a result, causes an increase in σ . A dissipation of elastic forces of the rubbery block to the glassy block in asymmetric miktoarm architectures has been described to account for enhanced mechanical properties of these systems.[215, 263] The consistent breadth of the

PI normal mode among all architectures within the lamellar morphology is congruent with the necessity for the chains to move cooperatively to maintain a constant segment density.[71, 119, 133] Furthermore, an increase in the normal mode intensity has been observed in polymer systems consisting of chains that are less confined.[120, 293, 294] Therefore, we attribute the changes in the PI chain relaxation shape for PSPI₂ in the lamellae to cooperative motion of individual PI chains enhanced by motional cross-correlation of chains sharing a common junction due to architectural asymmetry, compounded by the thermodynamic need for equalization of decreased conformational entropy near the interface by the elastic forces of the PI blocks to the junction with a glassy PS chain.

Conclusions

New insights are gained through a set of studies focused on chain dynamics of miktoarm star copolymer systems that form lamellar morphologies in the melt state at temperatures below the order disorder transition. The relaxation behaviors of these systems are compared to the well-established case of lamellar forming linear diblock systems. In the asymmetric PSPI₂ architecture, a change in the PI chain relaxation spectral shape reveals an increase in normal mode intensity which is attributed to a motional cross-correlation of end-to-end vector relaxations adding to the dielectric relaxation function due to the asymmetric architecture. This decreases the anisotropy of PI motion along the chain contour allowing them to move cooperatively relative to PI chains in the symmetric architectures of the PS₂PI₂ and linear diblock systems. We argue that this change in dynamics is promoted by the balance between elastic forces and decreased entropy near the junction point as suggested by the increase in area per junction point for this asymmetric miktoarm star architecture. These changes in equilibrium chain dynamics near the interface brought about by complex architecture point to a need to pursue further fundamental understanding of dynamical properties in phase separated block copolymer systems including those with complex architectures.

Given the importance of microphase segregated block copolymers having hard and soft blocks, these studies represent an important step in highlighting fundamental handles to advance the design and development of better thermoplastic elastomers.

Chapter 6: Dielectric Relaxations of Miktoarm Star Copolymers: Architectural Asymmetry

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Kinsey, T., *et. al.* *The effects of asymmetric molecular architecture on chain stretching and dynamics in miktoarm star copolymers.* *Macromolecules.* 2021. **54** (1): p. 183-194.

The polymers in this chapter were synthesized by WW under guidance from KH using methods developed by KH and JM at the CNMS. All of the polymers were prepared for measurement and measured by TK in the laboratory of SMK, JS or at Duke SMiF with help from Justin Gladman. The manuscript was primarily written by TK with edits, comments and revisions from EUM, SMK and JS. WW, KH and JM were the primary writers for the synthesis part of the Materials and Methods section.

Abstract

In this study, broadband dielectric spectroscopy and small-angle x-ray scattering are used to investigate the impact of architectural asymmetry on the dielectric polymer relaxations in seven miktoarm star copolymers. The miktoarm copolymers contain two identical poly(cis-1,4-isoprene) (PI) chains and one or two identical polystyrene (PS) chains (i.e. PSPI₂ or PS₂PI₂, respectively). The PI block molecular weight is varied across the copolymers to control morphology. The α and normal mode relaxation times for the PI chains are found to be unchanged compared to diblock PS-b-PI copolymers from the literature. However, in the architecturally asymmetric PSPI₂ systems, there is virtually no change in the

normalized dielectric strength or spectral shape of the chain relaxations across PI block molecular weight and morphology. This is in contrast with the trends among various morphologies for the PI chain relaxation spectral shapes and dielectric strengths both observed here for the symmetric 4-arm miktoarm polymers (PS₂PI₂) and reported for PS-*b*-PI systems. Additionally, a slow chain relaxation is measured in a 3-arm miktoarm copolymer with PS(PI-PS')₂ architecture even with both chain-ends of the PI chains embedded at the interface with the glassy PS block. These experimental results show that there are reduced constraints on PI chain dynamics for the PSPI₂ miktoarm architecture as predicted by the block copolymer Gaussian chain model with respect to chain stretching energies. We conclude that variations to molecular architecture in block copolymers can impact the dielectric chain relaxations which may be utilized to control macroscopic physicochemical properties in architecturally complex polymeric systems.

Introduction

In recent years, increased attention has been given to architecturally complex block copolymers (BCPs) due to remarkable properties that are attributed, either directly or indirectly, to the connectivity of the polymer chains.[210, 269, 295] Advances in synthesis techniques have afforded precise control over the BCP chain topology, which add molecular architecture as an additional molecular handle to tune the properties of these BCP materials.[211, 212, 261, 262, 264, 296] One such architecture is the miktoarm star copolymer, which is comprised of two or more blocks which contain multiple homopolymer chains, or “arms”, that are covalently connected at a central junction point.[213, 297] A particularly notable feature of the asymmetric miktoarm star copolymer (e.g. AB_n, which has one arm of polymer “A” as a block and “n” arms of polymer “B” as a block) is the reduced domain sizes that are formed during self-assembly with high molecular weight blocks compared to linear diblock copolymers with similar block molecular weights.[216] Additionally, intricate self-assembled morphologies that are less

accessible or not possible with for linear BCPs, such as “brick and mortar”, Frank-Kasper σ and A15 morphologies, have been reported to form due to architectural asymmetry in the miktoarm star copolymer. [104, 206, 227, 268, 298-302] In addition to morphological characteristics, BCPs with the miktoarm star architecture have displayed superior material properties compared to similar linear block copolymers, such as increased Young's modulus, elastic recovery, and enhanced ionic conductivity.[215, 226, 263, 268, 298, 303-312] The material properties that have been observed for the miktoarm star copolymers likely arise from the impact of the molecular architecture on the balance between morphology and dynamics. The dynamics of the polymer chains and segments within each block, which ultimately govern these properties, are extensively reported for linear BCP systems.[272, 313] However, the possible correlations between architecture and dynamics in BCPs remain speculative because few systematic studies have focused on the dynamical aspects of this class of materials. In this study we explore the relationships between BCP molecular architecture and dynamics while accounting for the chain stretching and interfacial energy effects of self-assembled phase separation and block molecular weight.

This work employed broadband dielectric spectroscopy (BDS) to probe the dynamics of poly (cis-1,4-isoprene) (PI) chains and segments in seven miktoarm star copolymers with glassy polystyrene (PS) counter blocks. The dynamic environments of the PI arms among the asymmetric 3-arm miktoarm polymers are compared to those among the symmetric 4-arm architectures. The polymers include three symmetric (A_2B_2) and three asymmetric (AB_2) miktoarm polymers, where “A” refers to the polystyrene [PS] block and “B” refers to the polyisoprene [PI] block, and the PI volume fraction ϕ_{PI} is increased within these two sets of three. The self-assembled microstructures and domain length-scales were measured using small-angle x-ray scattering (SAXS). We report the molecular architecture of the AB_2 miktoarm polymer effects the dielectric PI chain relaxation when compared to the effects of morphology on chain dynamics that are similar for the symmetric

A₂B₂ architecture and linear AB diblock systems from the literature. An additional miktoarm star copolymer with the PS(PI-PS')₂ architecture is compared, which has small molecular weight PS' blocks added to the PI chain ends which causes the PI chains to stretch across the interface compared to the asymmetric AB₂ architecture. The dielectric relaxations of the PI chains in these miktoarm star copolymers are discussed in terms of the balance between the chain stretching and interfacial energies which contribute to the overall free energy of BCP phase separation to better develop the relationship between block copolymer dynamics and molecular architecture.

Materials and Methods

Seven miktoarm star copolymers are measured in this study: three with the 3-arm miktoarm architecture PSPI₂ with one arm of PS and two arms of polyisoprene, three with the 4-miktoarm star architecture PS₂PI₂ with two arms of PS and two arms of PI, and one with 3-arm miktoarm architecture PS(PI-PS')₂ with one arm of PS connected to two diblock copolymer arms PI-PS'. The PS' indicates a different molecular weight as the main PS block. The characteristics of each copolymer are listed in Table 13. All of the polymers were prepared by anionic polymerization in all-glass reactors with break-seals, distilled benzene as the solvent and *butyl*-lithium as the initiator, as previously reported⁸⁷. These conditions are known to generate PI with high *cis*-1,4 microstructure (70% *cis*-1,4, 23% *trans*-1,4, and 7% 3,4) with monomeric dipole alignment converging to the primary junction point with the PS block.[261] Respective chlorosilane linking agents were used to control the chain topology in the miktoarm star copolymers.[262, 314] Absolute molecular weights were determined using size exclusion chromatography with THF as the mobile phase and a light scattering detector, using the appropriate specific refractive index increments (dn/dc).

Table 13: Characteristics of the miktoarm star copolymers investigated in Chapter 6

Architecture ID	Sample ID	Molecular weight (kg/mol)					ϕ_{PI}^a	$\bar{D}$
		$Mw_{PS,arm}$	$Mw_{PS,block}$	$Mw_{PI,arm}$	$Mw_{PI,block}$	$Mw_{PS'arm}$		
PSPI₂	18k-10k₂	18	18	10	20	--	0.565	1.05
	18k-18k₂	18	18	18	36	--	0.7	1.02
	18k-32k₂	18	18	32	64	--	0.806	1.01
PS₂PI₂	16k₂-9k₂	16	32	9	18	--	0.396	1.04
	16k₂-24k₂	16	32	24	48	--	0.636	1.01
	16k₂-52k₂	16	32	52	104	--	0.791	1.08
PS(PI-PS')₂	18k(12k-3k')₂	18	24	12	24	3	0.538	1.06

^a total volume fraction of PI in polymer by $x(x+y)^{-1}$ where $x = Mw_{PI,block} \rho_{PI}^{-1}$ and $y = Mw_{PS,block} \rho_{PS}^{-1}$ with $\rho_{PI}=0.83 \text{ g cm}^{-3}$ and $\rho_{PS}=0.969 \text{ g cm}^{-3}$

It is worth noting that the PS block of the PSPI₂ copolymers have been isotopically substituted (deuterium for hydrogen) for possible future neutron scattering and ¹H NMR studies. Differences between deuterated and non-deuterated PS have been shown to be negligible in self-assembled phase separation and in the dielectric response of the PI chains measured by BDS at temperatures below the dynamic glass transition temperature of deuterated PS ($T_g \sim 105^\circ\text{C}$).[315, 316]

Small-angle X-ray scattering (SAXS) measurements were performed using a SAXLab Ganesha instrument with a 50 kV Cu Xenocs Genix ULD point source and a 170 μm pixel, 20Hz Dectris Pilatus 300k detector at 25°C. The samples for SAXS measurements were hot pressed under N₂ atmosphere at 150 °C for 20 min to form a polymer film of $\sim 100\mu\text{m}$ thickness, annealed for 48 h at 430 K under N₂, then cooled to room temperature and sandwiched between two layers of Kapton tape. The scattering profile of Kapton was directly subtracted from the spectrum of each sample as a background.

A Novocontrol High Resolution Alpha Dielectric Analyzer equipped with a Quatro Cryosystem temperature control to make dielectric measurements with an applied electric field of 0.5 V in a frequency range of 10^{-1} - 10^6 Hz at temperatures from $220\text{ K} \leq T \leq 400\text{ K}$ at $10 \pm 0.2\text{ K}$ steps. Polymer films were prepared in the same manner as the SAXS samples, but rather than being sandwiched between Kapton tape they were sandwiched between two 10 mm brass electrodes with a fixed spacing using two 100 μm diameter silica rods, then annealed under N₂ atmosphere at 430 K for >18h. The polymers were then cooled to 290 K and the dielectric response was measured. In this study, only the dielectric data at $T \leq 360\text{ K}$ are presented and discussed. Due to the high T_g of the PS block, contributions from its segmental dynamics at $T \leq 360\text{ K}$ occur at frequencies slower than our experimental spectral window ($<10^{-1}\text{ Hz}$), allowing access to chain and segmental dynamics of the PI blocks tethered to the glassy PS interface.

Finally, a transmission electron micrograph (TEM) image of the 18k18k₂ and 18k32k₂ samples are included in Figure 63 to confirm the morphologies formed upon self-assembly, which are not conclusive from the SAXS profiles. This 100 nm sample was cryo-ultramicrotomed at -90°C after measurement by BDS. The sample was collected onto a 400 mesh copper TEM grid and stained with OsO₄ vapor (using a 4 wt% aqueous solution) for 3 hours. The sample was imaged using a Zeiss Libra 120 TEM (at the Oak Ridge National Laboratory, accessed through the CNMS User Program (proposal CNMS2017-418)).

Results and Discussion

In Figure 64 the SAXS profiles for the 18k-10k₂, 18k-18k₂, 18k-32k₂ and 18k(12k-3k')₂ polymers are plotted against the scattering vector, q . The 18k-10k₂ copolymer form lamellae 24.6 nm as discussed in Chapter 5. The 18k-18k₂ and 18k-32k₂ copolymers appear from the SAXS data to self-assemble into spherical PS morphologies in a continuous matrix of PI. To confirm the morphologies of these two polymers, TEM images were taken (see Fig. 63) where, in addition to PS spheres, some cylindrical domains are also observed for the 18k-18k₂ polymer.

The diameters of these spherical PS domains are $\sim 18 \pm 1.2$ nm for both of these polymers as calculated using

$$d_{\text{sph, PS}}(\text{SAXS}) = (4\pi/q^*)(2\phi_{\text{PI}}/\pi\sqrt{3}) \quad 88$$

where q^* is the scattering vector of the first Bragg peak and the ϕ is the volume fraction of PI for the 18k18k₂ and 18k32k₂.^[126] The spacing among PS spheres is larger and an increase in long range order is observed for the 18k-32k₂ copolymer as indicated by the SAXS peaks at higher q values and TEM images. This is understood by the 18k18k₂ polymer having a lower molecular weight and both spherical and cylindrical domains.

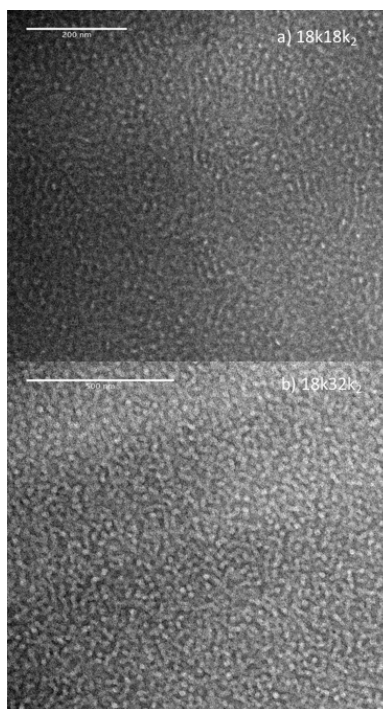


Figure 63: TEM images of PS phases (white) and continuous OsO₄-stained PI domain (dark) for the 18k18k₂ polymer which shows cylinders and spheres of PS (a) and 18k32k₂ which shows PS spheres (b).

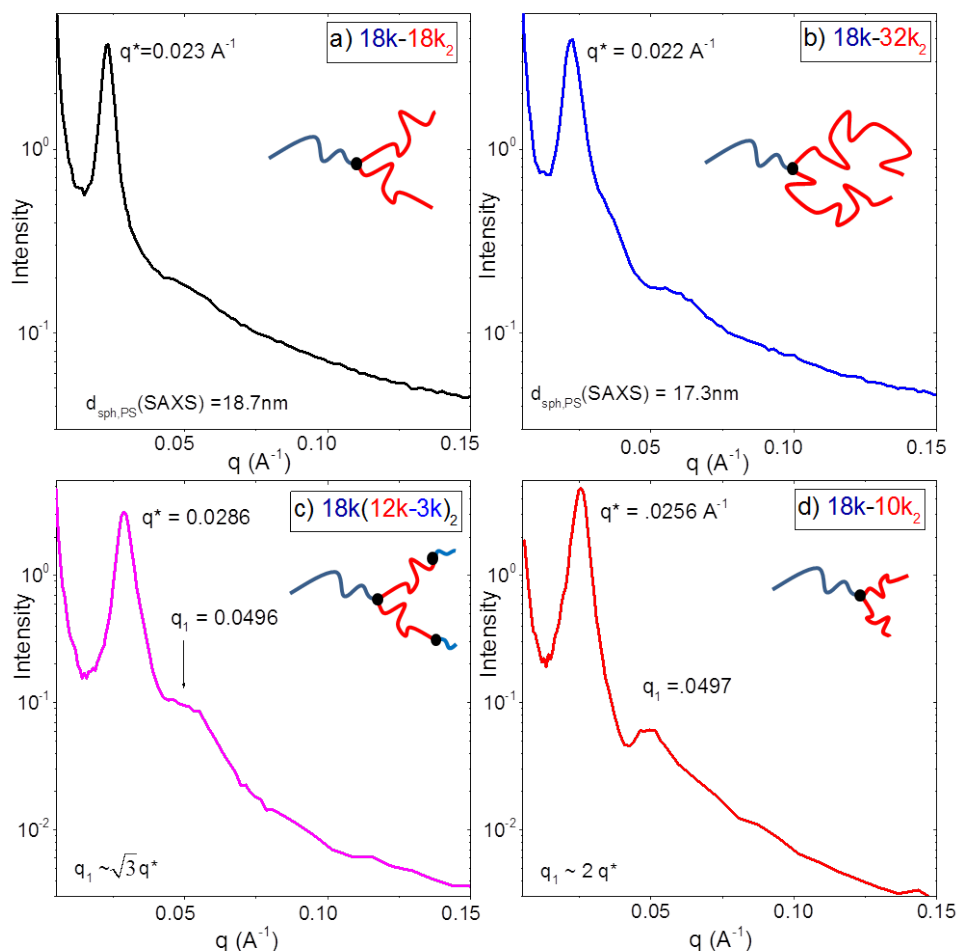


Figure 64: SAXS scattering profiles for the 3-arm miktoarm star copolymers. The 18k-18k₂ and 18k-32k₂ polymers (a, b) adopt a spherical PS morphology with similar PS domain sizes. The 18k(12k-3k')₂ polymer (c) forms PS cylinders. The 18k-10k₂ polymer forms lamellae and is also found in Chapter 3. A sketch of each polymer architecture is inset in each plot, with the blue indicating PS blocks and red indicating the PI block.

The $18k(12k-3k')_2$ copolymer forms PS cylindrical morphology as indicated by the higher order SAXS peak at $q = q^*$ in Figure 64c. For linear PS-PI diblock copolymers with $\phi_{PI} = 0.5$, lamella structures are typically expected. However, the $A(BA')_n$ architecture has been shown previously to form cylinders of the A block for $\phi_B = 0.5$. [98, 263, 309] To compare our $18k(12k-3k')_2$ copolymer to similar polymers from the literature, the block-asymmetry parameter ($T_{bi} = M_{PS} / [M_{PS} + M_{PS'}]$), which quantifies end-block bidispersity of the PS and PS' chains, is calculated to be $T_{bi} = 0.856$. This value suggests that there is no deflection in the cylinder-gyroid phase transition region, and corroborates the observed formation of the cylindrical morphology for the $18k(12k-3k')_2$ polymer. [309, 317, 318] Comparing the q^* values of the two 3-arm miktoarm star copolymers with $\phi_{PI} \sim 0.5$ in Figures 64c and 64d, q^* for $18k(12k-3k')_2$ is seen to be increased compared to the $18k-10k_2$ polymer. This corresponds to a larger distance between PS domains in the $18k-10k_2$ even though the $18k(12k-3k')_2$ polymer has a larger molecular weight PI block and suggests that in the $18k(12k-3k')_2$ system the PI chains are more stretched across the PI. This is analogous to the PI chains in a PS-PI-PS triblock copolymer, and will be discussed in more detail when dielectric relaxations of the $18k(12k-3k')_2$ copolymer are presented later in this chapter. [124]

For the three $PSPI_2$ miktoarm copolymers and the $PS(PI-PS')_2$ polymer, the microstructures are interpreted from the SAXS profiles in Figure 64. The SAXS profiles for the remaining polymers are found in Figure 65. The $16k_2-24k_2$ copolymer forms lamellae with a domain spacing of 33.2nm and is covered in Chapter 5. The $16k_2-9k_2$ copolymer forms ~ 10.6 nm PI spheres within a continuous PS domain using Equation 88 with ϕ for the PS volume fraction. The PI spheres in this polymer seem to be oriented with respect to the incident x-ray beam as shown in the asymmetric scattering in the 2D profile in Figure 66. The $16k_2-52k_2$ polymer displays scattering representative of PS cylinders within a continuous PI matrix due to $q_1 \sim \sqrt{3} q^*$ suggesting domains of PS cylinders within a continuous PI matrix.

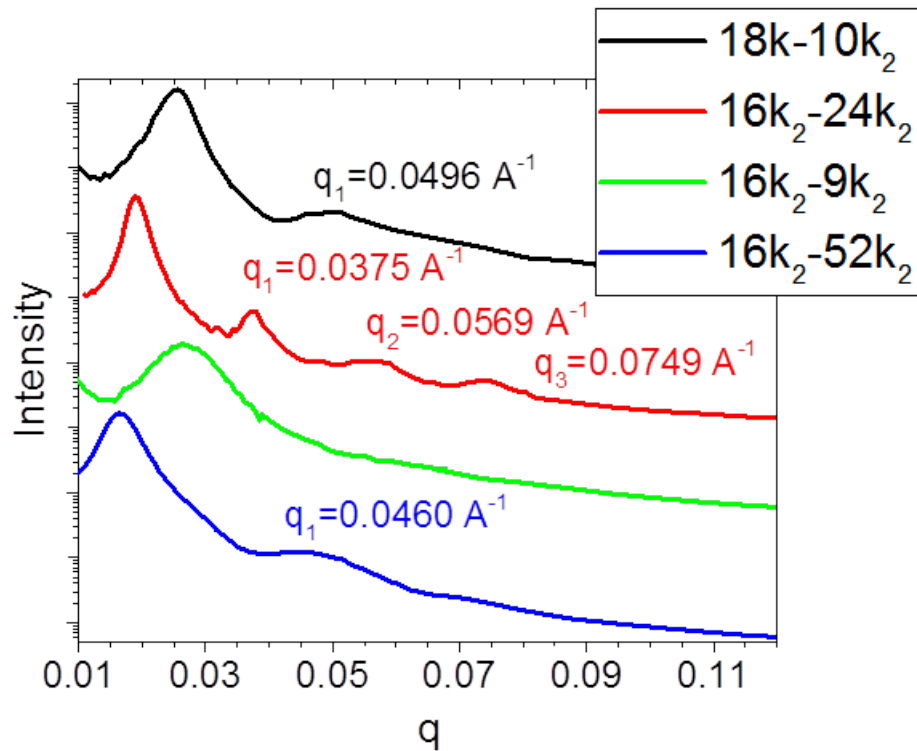


Figure 65: SAXS Profiles for the 4-arm miktoarm polymers and the 18k-10k₂ polymer. Q* peaks for the 18k10k₂, 16k₂24k₂, 16k₂9k₂ and 16k₂52k₂ polymers occur at 0.0256 Å⁻¹, 0.0194 Å⁻¹, 0.0263 Å⁻¹, and 0.0164 Å⁻¹, respectively. Higher order peaks are noted in the figure with colors corresponding to the respective data.

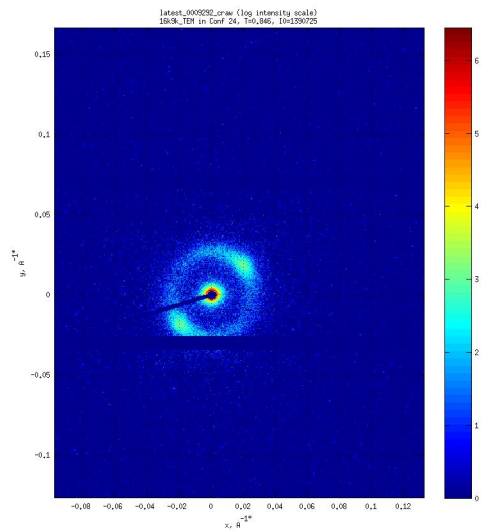


Figure 66: 2D scattering profile for the 16k₂-9k₂ polymer. The nonuniform scattering in all directions suggest that the spherical domains are preferentially ordered with respect to surface normal to the incident beam.

Lastly, the PI block molecular weight dependence of the q^* values are plotted in Figure 67 where these values are observed to decrease with increasing block molecular weight for all polymers, and decrease faster for the 4-arm miktoarm copolymers. This is in agreement with previous reports of smaller domain spacings observed for the asymmetric miktoarm architecture.[216, 277]

For dynamics of the PI chains with a high *cis*-1,4 isomeric chemical structure, which is considered a model Type-A polymer, the time dependent dielectric response function is related to the complex permittivity by

$$\varepsilon^* - \varepsilon_\infty = -\Delta\varepsilon \int_0^\infty \frac{d}{dt} \Phi(t) e^{-i2\pi f t} dt \quad 89$$

where ε_∞ is the high frequency (unrelaxed) value of the real part of the dielectric function, $\Delta\varepsilon$ is the dielectric relaxation strength and f is the frequency of the applied electric field. The alignment of the monomeric dipole moments within the backbone of a Type-A chain are such that they may be separated mathematically into vectors that are perpendicular ($\mu^\perp$) and parallel ($\mu^\parallel$) to the chain contour.[89, 91]

In the imaginary part of the complex permittivity of polyisoprene, the averaged polarization responses of $\mu^\perp$ are observed as a high-frequency, low-temperature segmental process (*i.e.* α -relaxation) and the summation of the individual dielectric relaxations of $\mu^\parallel$ are observed as the normal mode process (*i.e.* chain relaxation) at lower-frequencies. When the timescales of these two relaxations are well separated, is described by a linear combination of the normalized autocorrelation function of the polarizations of the n^{th} and m^{th} segmental dipole vectors separated into $\mu^\perp$ and $\mu^\parallel$ portions across all chains by

$$\Phi(t) = \sum_i \frac{\sum_n \sum_m \langle \mu_i^\parallel(n;0) \cdot \mu_i^\parallel(m;t) \rangle + \sum_n \sum_m \langle \mu_i^\perp(n;0) \cdot \mu_i^\perp(m;t) \rangle}{\sum_n \sum_m \langle \mu_i^\parallel(n;0) \cdot \mu_i^\parallel(m;0) \rangle + \sum_n \sum_m \langle \mu_i^\perp(n;0) \cdot \mu_i^\perp(m;0) \rangle} \quad 90$$

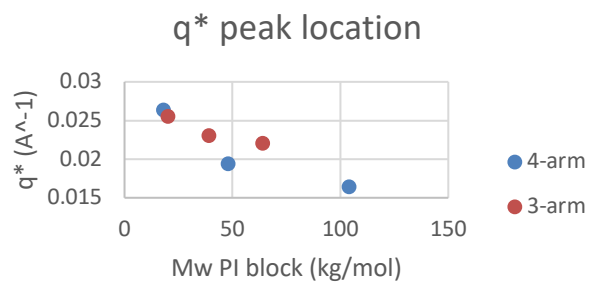


Figure 67: The q values for the lowest Bragg peak (q^*) for all miktoarm polymers plotted against the molecular weight of the PI block.

In Eqn. 90, the first term represents the averaged relaxation of the chain end-to-end dipole and occurs on the timescale of polymer flow, and the second term represents the averaged relaxation of segmental dipole vectors on the timescale of the dynamic glass transition. Cross terms between the polarization of dipoles within a single chain have been experimentally shown to be negligible due to the low dipole interaction energies relative to the thermal motion of the segments.[92] As for the local correlation function $C(n, t; m) = \langle \mathbf{u}(n; 0) \cdot \mathbf{u}(m; t) \rangle / \langle \mathbf{u}^2 \rangle$, cross-correlations among the dynamics and orientations of bond-vectors $\mathbf{u}(t)$ in a neighboring chain (as opposed to *polarization* cross-correlations of dipoles) may not vanish due to constraints on chain motion such as chain entanglements or phase separation in block copolymer systems. Often these orientational correlations are considered within the Kirkwood-Fröhlich correlation factor g , which is contained within the $\Delta\epsilon$ term in Eq. 88.[142, 319] This will be discussed further with Eqn. 96 in mentioned with respect to the $18k(12k-3k')_2$ polymer. For now, all dipole motion and orientations are assumed to be incoherent where g is unity.

All of the dielectric data for the miktoarm star copolymers (except for the $PS(PI-PS')_2$ polymer) were initially analyzed by creating a mastercurve with a reference temperature by shifting the dielectric loss data at each temperature (240K-330K) by a shift factor aT . [92] The temperature dependent shift factors for the 3-arm miktoarm star polymers are displayed in Figure 68. The shift factors for the 4-arm systems follows that for the linear diblock system. The resulting master curves are displayed in Figure 69. This representation shows that the frequency-temperature superposition principle holds for all of these systems. The analysis of the mastercurves allows the segmental and chain relaxations to be fit over a wide frequency range, and suggest the spectral shapes (not necessarily the intensity) of both relaxations are constant with temperature within the temperature range.

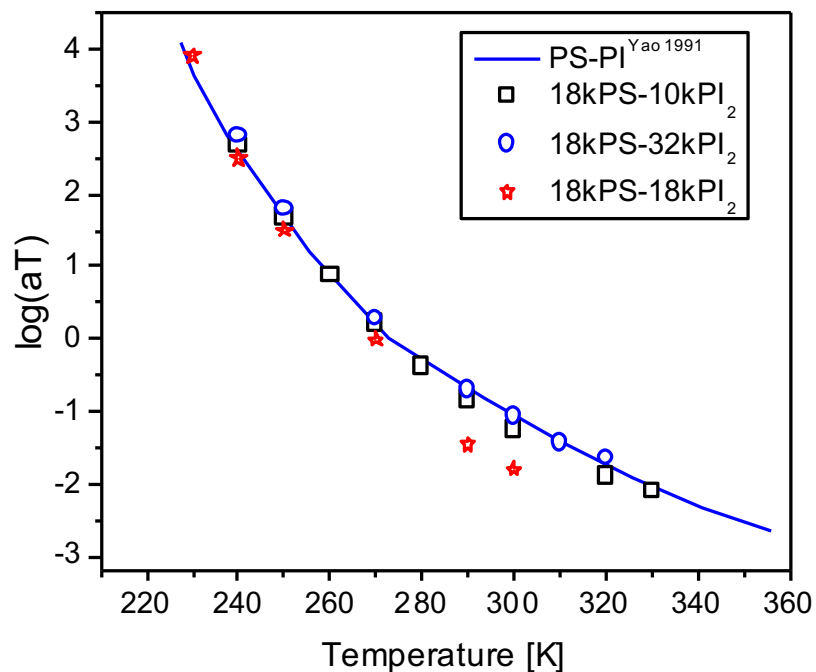


Figure 68: Frequency-temperature superposition shift factors at each temperature for the three 3-arm miktoarm star polymers in Chapter 4. The aT are similar to that observed previously for lamellar forming PS-PI linear diblock copolymers displayed as a line.[92]

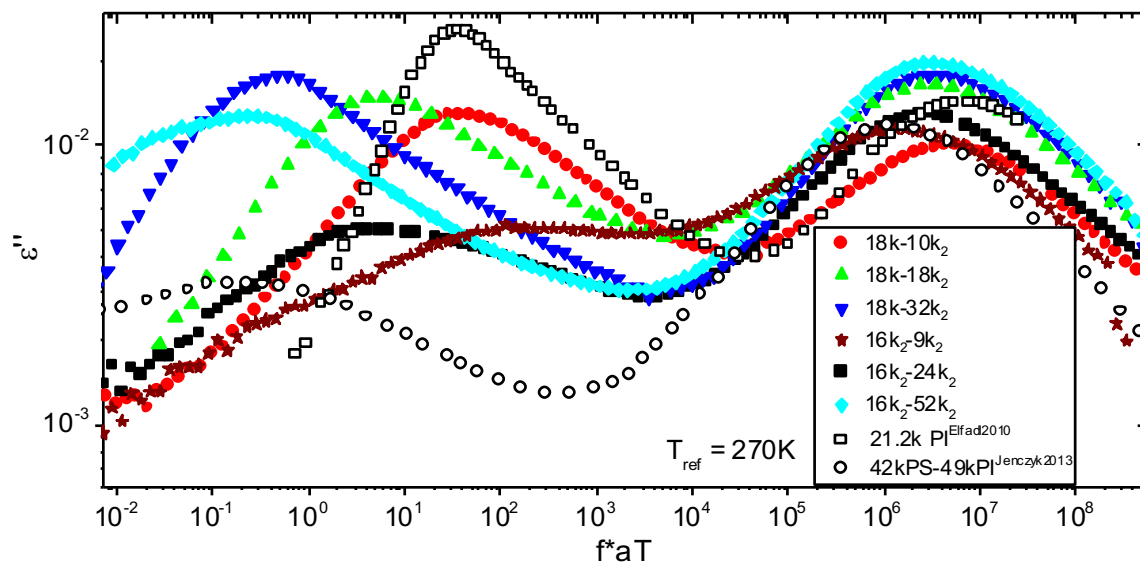


Figure 69: Dielectric loss from 240-330K shifted by aT factor to give the Frequency Temperature Superposition representation for all miktoarm polymers, and a linear diblock copolymer[119] (lamellar) and PI homopolymer[46] from the literature. The reference temperature of 270K is used with aT values taken from those used for PI homopolymer[92] or from Fig. 68.

The production of these master curves confirms that the PI chain and α relaxations are well-separated in the time domain (*c.f.* Eqn. 90) and the spectral shapes of each relaxation are constant with temperature.[119] The master curve spectra for the PS₂PI₂ and PSPI₂ polymers were fit for each polymer a linear combination of two individual Havriliak-Negami functions to reveal the spectral shapes of individual relaxations.

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \Delta\varepsilon_{HN}(1+(i\omega\tau)^{\alpha})^{-\beta} \quad 91$$

The variables in Eqn. 91 are $\Delta\varepsilon_{HN}$, τ_{HN} , α and β , which are the dielectric strength of the relaxation, the relaxation rate, and symmetric and asymmetric stretching parameters (*e.g.* shape parameters), respectively. The ω ($=2\pi f$) is the angular frequency of the applied electric field, ε_{∞} is the high frequency value of the real part of the complex permittivity ε^* . For the segmental relaxation, $\Delta\varepsilon_{HN}$ and τ_{HN} are termed $\Delta\varepsilon_{\alpha}$ and τ_{α} , respectively. For the chain relaxation, $\Delta\varepsilon_{HN}$ and τ_{HN} are termed $\Delta\varepsilon_n$ and τ_n , respectively. The fitting parameters for all PI chain relaxations in the miktoarm star copolymers in this study are in the Table 15.

Using the fitting parameters in Table 15, the dielectric loss was then fit to the spectra at each temperature. The chain relaxation for the 16k₂-52k₂ and 18k(12k-3k')₂ polymers were determined at each individual temperature to confirm the chain relaxation rates without prior understanding of the shape parameters due to conductivity contributions to the spectra toward lower frequencies and Eqn. 91 See Figures 70 and 71 for analysis of dielectric spectra of 16k₂-52k₂ and 18k(12k-3k')₂ polymers, respectively. At higher temperatures for the PS₂PI₂ and PSPI₂ polymers, the low frequency dc conductivity contribution to the spectra is described using $\varepsilon''(\omega) = \sigma_0(\omega \varepsilon_0)^{-1}$ where σ_0 is the dc conductivity, ε_0 is the vacuum permittivity and f ($=2\pi\omega$) is frequency in Hz.

Table 14: HN phape parameters to the PI segmental and chain relaxations of the miktoarm star copolymers in Chapter 6.

Polymer ID	α (segmental)	β (segmental)	α (chain)	β (chain)
16k ₂ -9k ₂	0.54 ($\pm$ 0.02)	0.71 ($\pm$ 0.02)	0.34 ($\pm$ 0.02)	0.96 ($\pm$ 0.02)
16k ₂ -24k ₂	0.65 ($\pm$ 0.03)	0.6 ($\pm$ 0.03)	0.58 ($\pm$ 0.03)	0.26 ($\pm$ 0.03)
16k ₂ -52k ₂	0.62 ($\pm$ 0.04)	0.68 ($\pm$ 0.04)	See Fig. 70	
18k-10k ₂	0.63 ($\pm$ 0.02)	0.59 ($\pm$ 0.02)	0.54 ($\pm$ 0.03)	0.75 ($\pm$ 0.03)
18k-18k ₂	0.58 ($\pm$ 0.05)	0.75 ($\pm$ 0.05)	0.55 ($\pm$ 0.02)	0.7 ($\pm$ 0.02)
18k-32k ₂	0.65 ($\pm$ 0.04)	0.6 ($\pm$ 0.04)	0.63 ($\pm$ 0.05)	0.78 ($\pm$ 0.05)
18k(12k-3k') ₂	0.63 ($\pm$ 0.03)	0.58 ($\pm$ 0.03)	See Fig. 71	

At higher frequencies to the PI chain relaxation, the overlap of the chain and segmental relaxations was analyzed such that the subtraction of the HN function for the PI α -relaxation results in a high frequency Debye-like cut-off of the chain relaxation in accordance with negligible cross-correlations between the $\mu^{\parallel}$ and $\mu^{\perp}$ in Eqn. 90.[46] This cutoff is observed from the analysis for the 18k18k₂ and 18k32k₂ polymers in Figure 72.

For such low ϵ'' intensities of the chain relaxation at frequencies that overlap with the α relaxation, the shape of each relaxation is not affected by subtraction of an HN function fit to the corresponding dielectric process. Equation 6.5 is used calculate the rate of maximum loss ($\omega_{\alpha, \max}$ or $\omega_{n, \max}$) for corresponding HN fits to the α or chain relaxation, respectively using the fitting parameters from Eqn. 91, and these rates are plotted in Figure 73.

$$\omega_{\max} = 2\pi T_{HN}^{-1} [\sin(\pi\gamma/2(\alpha+1)) / \sin(\pi\gamma\alpha/2(\alpha+1))]^{-\gamma} \quad 92$$

The HN fits for the PI chain relaxation to the master curve data in Figures 69 and 72 are subtracted from the spectrum, then the data is normalized by the peak value and the frequency of that value. This allows the shapes of the α =relaxation to be compared qualitatively.

The top panel of Figure 73 shows the temperature dependent frequency of maximum loss of the α relaxation from Eqn. 92. The shapes (shown in the bottom panel of Fig. 73) and rates are similar to the α -relaxation shape and peak frequency as PI in phase-separated diblock systems. The similarity in α -relaxation rates and spectral shapes among all of the polymers suggests that all PI segments within a block experience comparable localized environments with the same local friction coefficient within the phase-separated domains.[320] Therefore, the miktoarm architectures in this study do not affect molecular motion associated with the length-scales of the PI segments and, therefore, do not significantly affect the dynamic glass transition of the PI blocks.[285, 321, 322]. The rates of the chain relaxation will be discussed later in this chapter.

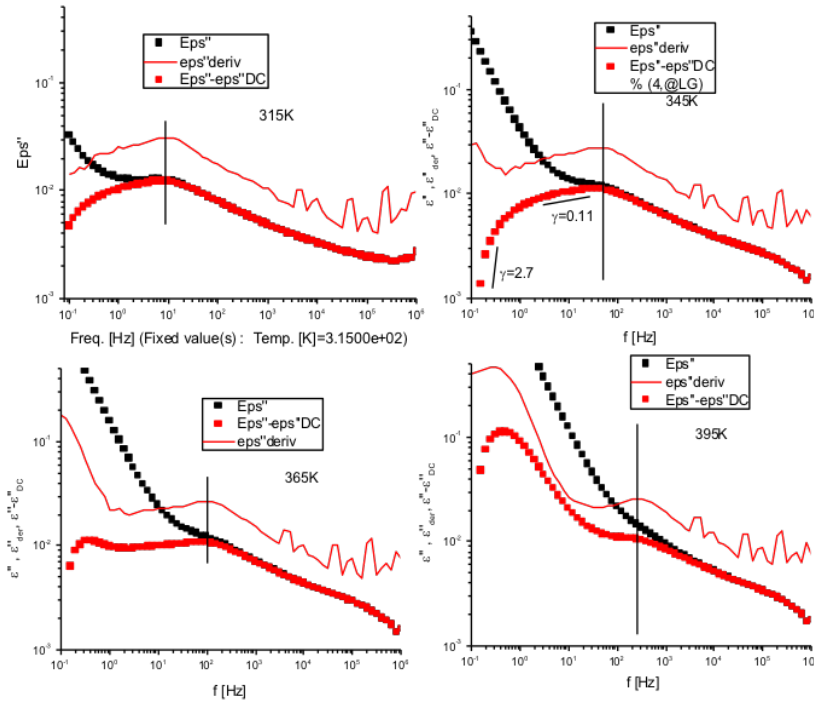


Figure 70: To determine the higher temperature chain relaxation rates, the dielectric loss (black squares) spectra at four different temperatures (a-d, identified on the plot) are shown for the 16k₂-52k₂ polymer. While the FTS principle holds, the peak maximum of the chain relaxation is difficult to observed due to a strong interfacial polarization process toward low frequencies (described by $= \sigma_0(\omega)^{-1}$) which is subtracted from the data (red squares). In addition to subtracting the conductivity contribution, the frequency of maximum loss for the chain relaxation is more clearly observed when calculating the from the Kramers-Kronig relation (red line) through $\epsilon''_{\text{der}} = -\pi/2[\partial\epsilon'/\partial\ln(\omega)]$.

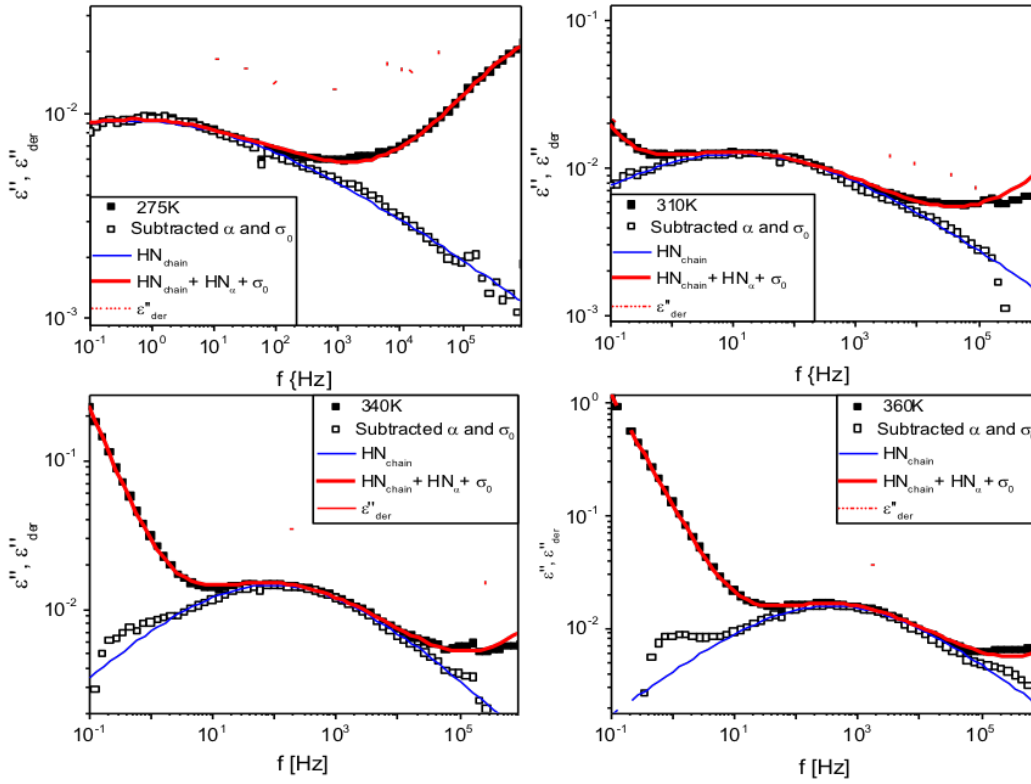


Figure 71: Dielectric loss at four temperatures for the 18k(12k-3k')₂ polymer (filled squares). The HN fits for the chain relaxation is observed as a blue line. The contribution to the spectrum at higher frequencies (segmental relaxation) and lower frequencies (conductivity) are fit with a HN function and with $\epsilon''_{\sigma_0} = \sigma_0(2\pi f\epsilon_0)^{-1}$, respectively. The fits for these contributions are subtracted from the data revealing the chain relaxation (open squares) to show the accuracy of the chain relaxation HN fit. The dotted red line is the representation calculated from the Kramers-Kronig relation ($\epsilon''_{der} = -\pi/2[\partial\epsilon'/\partial\ln(\omega)]$) which suppresses conductivity contributions to the loss spectra. Each temperature was fit individually due to the change in the spectral shape of the chain relaxation as described in the main text.

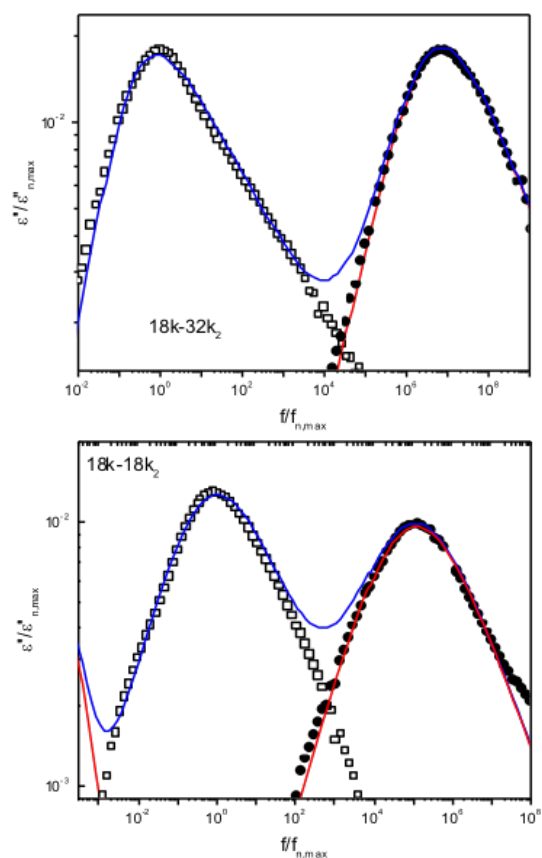


Figure 72: Analyses of the dielectric loss in the frequency-temperature-superposition representation for the 18k-32k₂ (top) and 18k-18k₂ (bottom) miktoarm polymers are performed by fitting the chain and segmental relaxations (low and high frequencies, respectively) each with the empirical Havriliak-Negami function (Eqn. 91). First, the segmental relaxation is fit with a HN function (red line). This data was then subtracted from the spectrum to reveal the shape of the dielectric chain relaxation (open squares). This chain relaxation is then also fit with a HN function. A linear combination of the two HN fits are observed as the blue line. Subtracting this chain relaxation HN fit from the data reveals the segmental relaxation (closed circles).

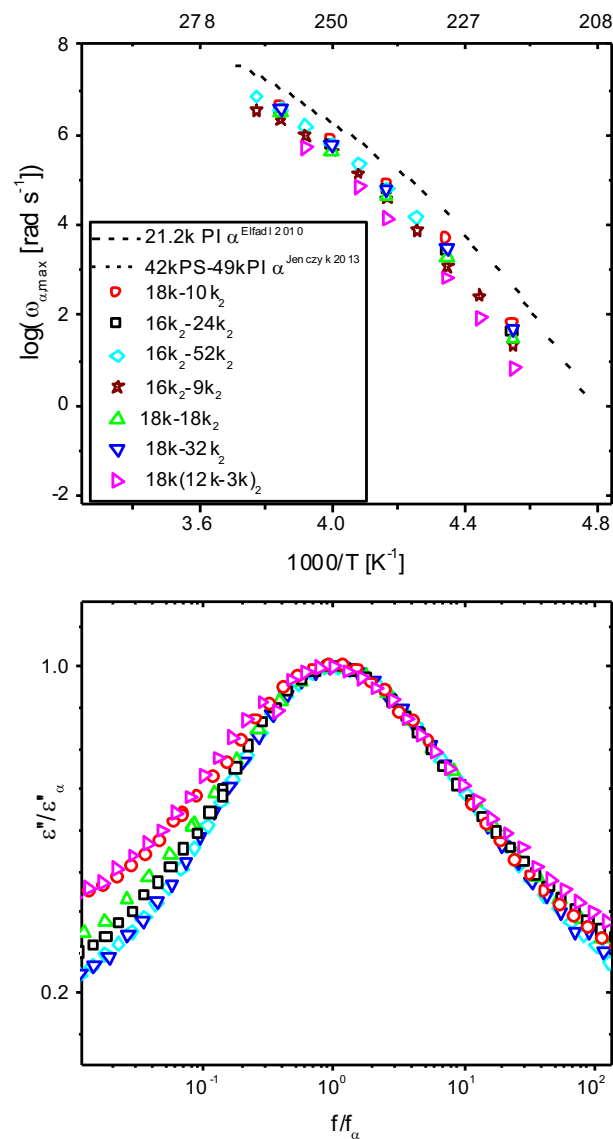


Figure 73: Segmental (α -) relaxation rates of PI plotted for all miktoarm star polymers in this study (top). Additionally, the α relaxation rates for the PI homopolymer and PI in a lamellar forming PS-PI linear diblock copolymer are included from the literature[46, 119]. The PI dielectric loss corresponding to the α relaxation is normalized by maximum loss and frequency for all miktoarm star polymers displaying similar spectral shapes. This implies a similar distribution in relaxation times for this process, and that all PI segments have the same local frictions for this segmental motion.

The normal modes for the PS_2PI_2 and PSPI_2 polymers are revealed by subtracting the HN fit to the segmental relaxation from the master curve data. In Figure 74 the spectral shapes of the dielectric chain relaxations of the PSPI_2 polymers are normalized by PI volume fraction (ϕ_{PI}) and the frequency of maximum loss (f_n). The shapes and intensities of these processes are very similar, even with increasing molecular weight and differences in morphologies among these polymers. This suggests that similar normal modes are contributing to the dielectric chain relaxation for these polymers.[136] On the other hand, the spectral shapes of the chain relaxations for the 4-arm miktoarm copolymers (PS_2PI_2) vary drastically among the samples, as shown in Figure 75.

The PI chain relaxation shapes for the PI spherical and PS spherical morphologies for the $16k_29k_2$ and $16k_252k_2$ polymers, respectively, are similar to the relaxations observed for PI linear diblocks with the same morphologies as displayed in Figure 76, and discussed in Chapter 3. The trend in PI chain relaxation shape for different morphologies has been described in the following way: As constraints on chain motion are increased due to changes in morphology resulting in a slowed relaxation time and decrease in peak intensity of the relaxation process which spans a wider frequency range (often termed “broadening” of the terminal relaxation).[133, 137] The reported trend follows an increase in spectral broadening as the morphology changes from a continuous PI domain $\rightarrow$ lamellar $\rightarrow$ PI cylinders $\rightarrow$ PI spheres based on block volume fractions.[126] Spectral broadening is associated with increased orientational anisotropy of chain conformations and dynamic anisotropy along the chain contour with respect to the normal vector from the domain interface, as well as increased thermodynamic constraints.[125, 126, 323] The thermodynamic, or “osmotic”, constraints are expressed as the requirement to maintain a constant segment density within the domain and as these constraints increase, there is a decrease in the available chain configurations (*i.e.* decrease in entropy).[92]

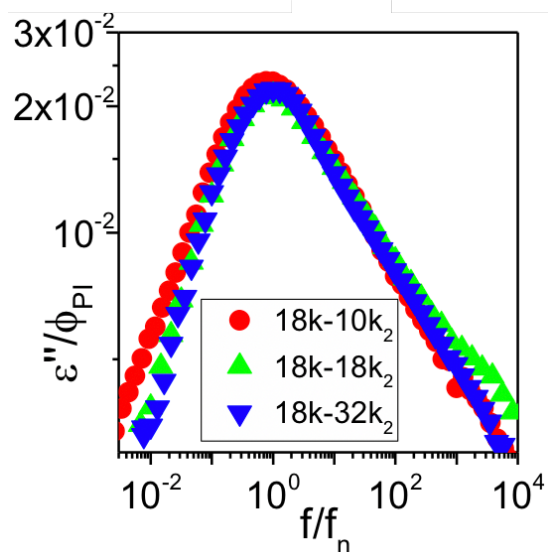


Figure 74: The spectral shapes of chain relaxation spectra for the PSPI₂ polymers are presented by normalizing by PI volume fraction (ϕ_{PI}) and frequency by the frequency of maximum loss (f_n) to facilitate comparison of the relaxation shapes.

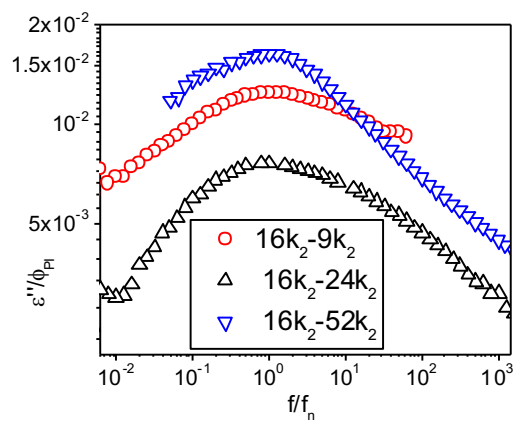


Figure 75: Dielectric loss spectra of PI chain relaxations normalized by PI volume fraction (ϕ_{PI}) for the three 4-arm miktoarm polymers (PS₂PI₂) in our study.

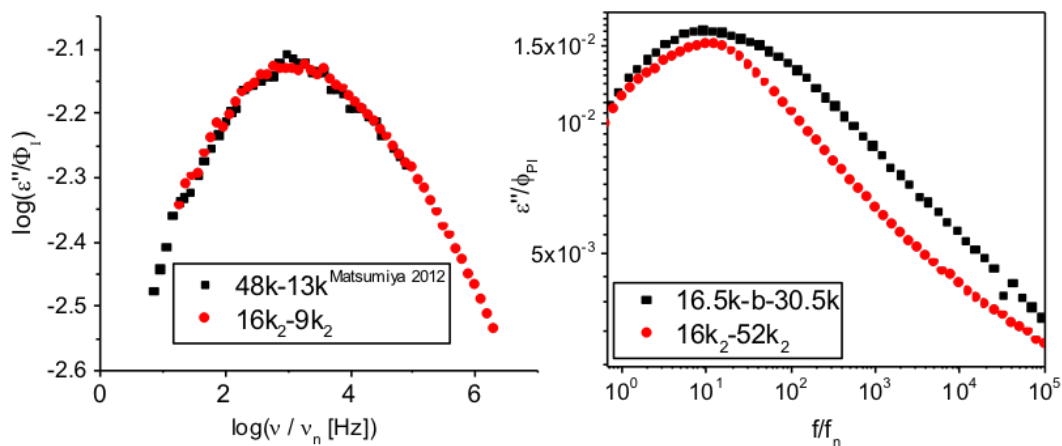


Figure 76: Normalized dielectric loss corresponding to chain relaxations for 16k₂-9k₂ miktoarm polymer compared with that for a PI-sphere forming linear PS-PI diblock (Left)[126], and for 16k₂-52k₂ miktoarm polymer compared with a linear PS-PI diblock with similar continuous PI domain that we measured ourselves (Right).

Within the framework of the monodisperse homopolymer Gaussian chain model outlined in Chapter 2, the coarse grain segments take on random configurations in all directions. On the other hand, for the Gaussian chain in phase-separated block copolymers, introduced in Chapter 3, there is an increased segmental stretching required to maintain a constant density within the domain causing a decrease in the number of available configurations.[101] In the strong segregation limit, the area per molecule within the interface is directly proportional to the free energy of mixing that is required to maintain the interface and inversely related to the stretching energy that is imposed by elastic forces on the junction points. These two contributions constitute the total free energy that drives phase separation.[101]

The total free energy (F) of a phase separated block copolymer system is increased compared to that described by the homopolymer Gaussian coil in order to maintain the order of phase separation. Two additional contributions to F are the interfacial energy (i.e. excess energy compared to the homopolymer required to maintain the interface) and energy of chain stretching (i.e. excess energy from the Gaussian coil due to orientational anisotropy). These two additional terms are described by Matsen as a counterbalance in order to minimize F at equilibrium as shown by the free energy of an incompressible, lamellar forming block copolymer system by

$$\frac{F}{nk_B T} = \Sigma \rho_0 b (\chi/6)^{1/2} + \Sigma_{blocks} \frac{\pi^2 N}{8 \Sigma^2 \rho_0^2 b^2} \quad 93$$

where n is the number of molecules, k_B is the Boltzmann constant, T is absolute temperature, Σ is the interfacial area per molecule ($\Sigma=A/n$, with A as the interfacial area), ρ_0 is the segment density, b is the statistical segment length, χ is a proportionality constant equivalent to the Flory-Huggins interaction parameter and N is the total number of segments in the polymer block[101]. Note this is very similar to Watanabe's use of the Zhulina-Halperin self-consistent field theory model for lamellar ABA triblock copolymers[124]. The first term represents the free energy

of the interface, which is analogous to the free energy of mixing. The second term is the chain stretching energy, which is also termed the elastic free energy, and can be split into a sum of the two individual blocks for a diblock system. To minimize the total free energy, there is a counterbalance between a large Σ that minimizes the stretching energy and a small Σ which minimizes the interfacial energy. It was determined in Chapter 5 that the 3-arm miktoarm system has an increased area per molecule at the lamellar interface which corresponds to a reduced chain stretching portion of the total free energy. The equilibrium area per molecule is determined at the minimum of the total free energy in Eqn. 94 below.

$$\Sigma = \frac{N^{1/2}}{\rho_0 b^2} \left(\frac{3\pi^4}{8\chi N} \right)^{1/6} \quad 94$$

Substituting Eqn. 94 into Eqn. 93 shows that the equilibrium stretching energy is half the equilibrium interfacial energy. It has been determined that the asymmetric architecture of the AB_n miktoarm polymers have an increased χ parameter and an increased area per molecule. Therefore, from Eqns. 93 and 94 there is a decreased stretching energy in the architecturally asymmetric systems compared in the to block copolymers with symmetric architectures. The differences in the osmotic constraint on PI chain motion that is required to maintain constant segment density among differing domain geometries are reduced for the $PSPI_2$ polymers. The reduced osmotic constraint then causes a decrease the orientational anisotropy of chains with respect to the interface resulting in similar dielectric normal mode spectral shapes in Figure 74 for the three $PSPI_2$ polymers.

Now is the time to return to incorporating the data for the $18k(12k-3k')_2$ polymer. The chain relaxation for this polymer has a temperature dependent shape, and, therefore, a master curve could not be prepared from the dielectric data. Consequently, the chain relaxation was fit individually for each temperature without an initial estimate of the shape parameters. The segmental relaxation shape is constant and the fits at four temperatures with segmental relaxation HN

fit and conductivity subtracted from the data are shown in Figure 71. Also, to confirm the relaxation rates, the Kramers-Kronig relation is used to calculate the dielectric loss data from the real part of the complex permittivity by $\epsilon''_{\text{der}}(\omega) = -2/\pi [d\epsilon'/d \log \omega]$ which suppresses the high-temperature, low-frequency conductivity contribution, and the frequency of maximum loss is determined without and HN fit. The chain relaxations revealed from this analysis for the 18k(12k-3k')₂ copolymer are presented at each individual temperature in Figure 77 where a slow dielectric relaxation is observed at the selected temperatures. In block copolymer systems where both ends of the PI chain without dipole inversion are tethered to the glassy PS interface, it is expected that no chain relaxation would be observed.[56, 125]

There are two possible mechanisms giving rise to the observed dielectric PI chain relaxation in PS(PI-PS')₂: 1) there are fluctuations of the two PI chain ends that share the junction point with the PS block, or 2) there are fluctuations at the PI chain ends connected to the PS' block, possibly due to melting of the low molecular weight PS' chains. Mechanism 2 has been described elsewhere as A' block "pull-out".[298, 309, 317]

To verify whether the second mechanism is plausible for the 18k(12k-3k')₂ system, the scattering invariance (Q) was determined from the Kratky plot in Figure 78, which provides the degree of electron density contrast across the interphase (see Table 15 for values of Q).[324] When there are only two phase-separated domains, the invariance is defined as $Q = \phi(1-\phi) \langle \eta^2 \rangle$, where ϕ is the volume fraction of either of the blocks and η is the difference in the electron density between the two phases.[325] The 18k(12k-3k')₂ copolymer and the 18k-10k₂ copolymer have nearly the same Q values (1.7×10^{-5} a.u./Å³ and 1.6×10^{-5} a.u./Å³, respectively), which suggest a similar contrast in electron density between the phases for the two polymers. Additionally, higher values of $I(q) q^4$ at long q (termed the Porod Plot found in Figure 79) are associated with decreased thickness of the interface between scattering domains.[326]

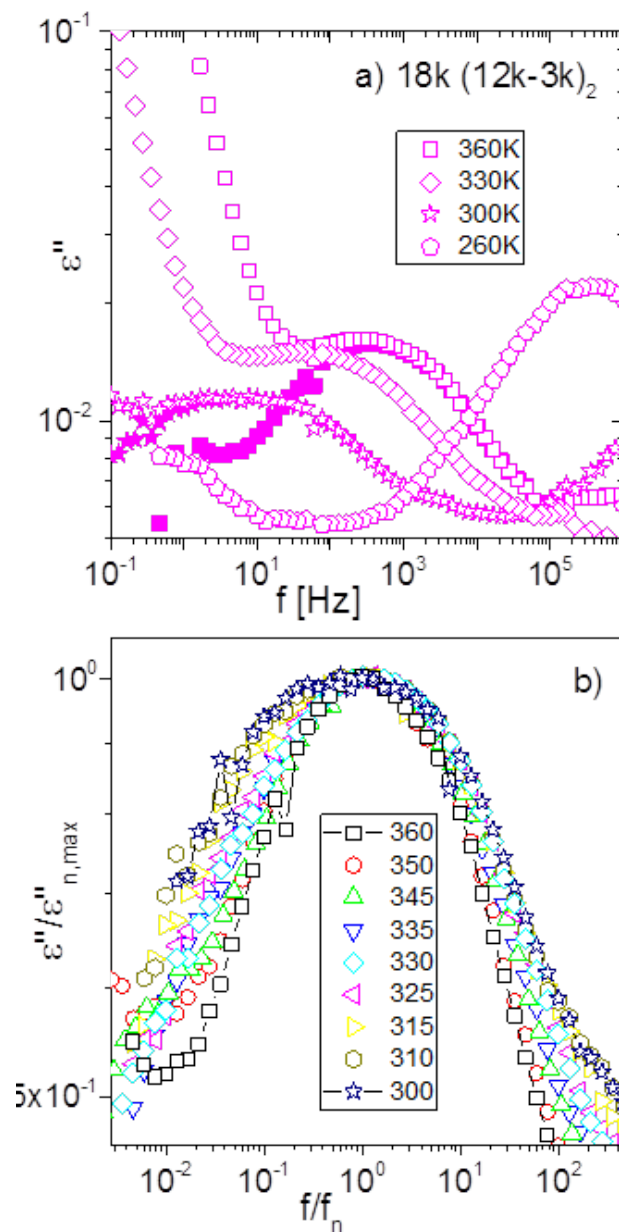


Figure 77: Dielectric loss at various temperatures as indicated for $18k(12k-3k')_2$ (open symbols) and modified dielectric loss spectra obtained by subtracting the ionic conductivity contribution at low frequencies (closed symbols) (a). In addition, the chain relaxations have been normalized by peak intensity and frequency to show a narrowing of the shape with increasing temperature (b). The error bars are smaller than or equal to the sizes of the data symbols.

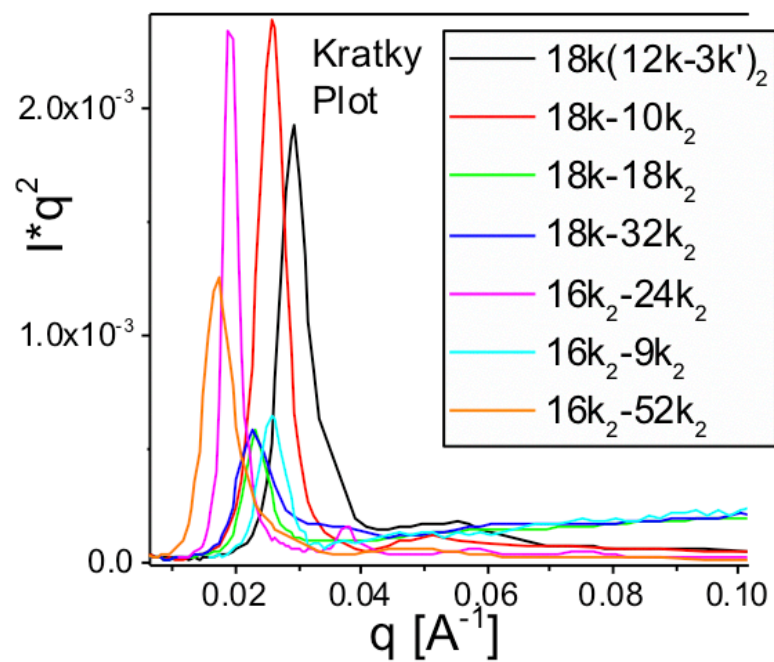


Figure 78: Kratky plot of the scattering data for all miktoarm star copolymers. Integration of these data give the scattering invariant and is a relative estimate of electron density change. The values of this integration are tabulated in Table 15.

Table 15: SAXS Invariance for miktoarm star copolymers

Sample	$Q \text{ (a.u. } \text{\AA}^3) = \int_{0.01}^{0.1} I(q) q^2 dq$
18k(12k-3k')₂	1.68E-05
18k-10k₂	1.65E-05
18k-18k₂	1.00E-05
18k-32k₂	8.84E-06
16k₂-24k₂	6.09E-06
16k₂-9k₂	3.90E-06
16k₂-52k₂	3.83E-06

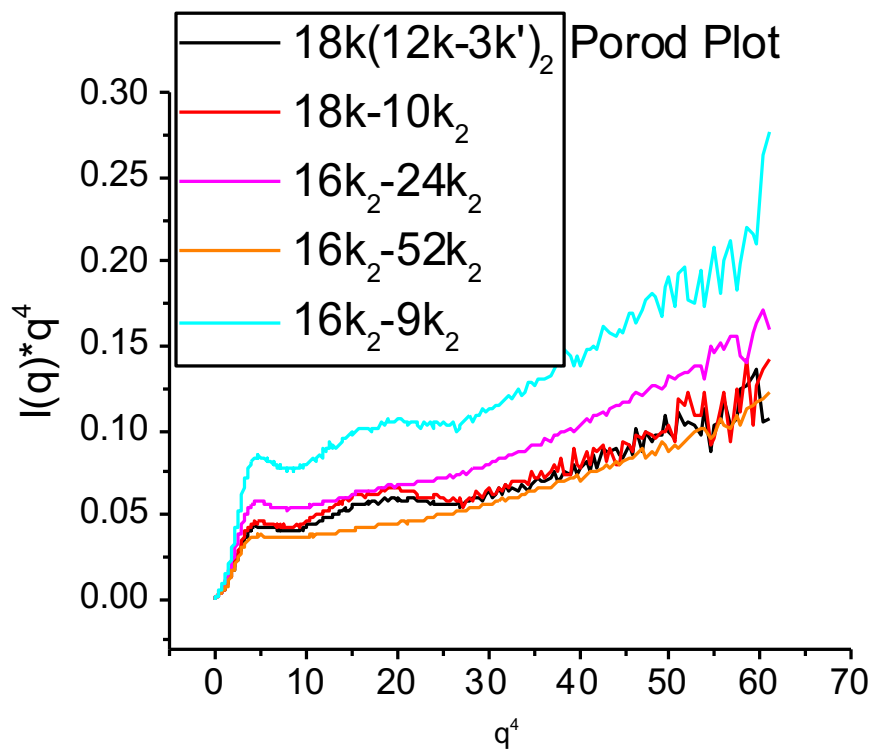


Figure 79: The Porod Plot of the SAXS profiles for miktoarm polymers. Limit of $I(q) \cdot q^4$ at high q values is associated with the relative thickness of the scattering interface. Smaller values at high q values correspond to decreased thickness of the interphase.

The ratio of $I(q) q^4/Q$ as $q \rightarrow \infty$ gives a relative estimate of the geometric surface area to volume ratio of the domain [326]. The 18k(12k-3k')₂ copolymer and the 18k-10k₂ copolymer have the lowest $I(q) q^4/Q$ values as $q \rightarrow \infty$ compared to the other polymers in this study. These results indicate sharp changes from PI to PS domains for the 18k(12k-3k')₂ and the 18k-10k₂ copolymers with a relatively narrow domain boundary thicknesses and suggest that the short PS' block remains segregated from the PI domain and is imbedded within the PS domain at room temperature. Therefore, we conclude that no “pull-out” occurs for the 18k(12k-3k')₂ copolymer at the temperature of the SAXS measurement.

Next, to address a possible PS' pull-out at other temperatures, we note the similarity in the temperature dependence of $\omega_{\alpha, \max}$ among all of the block copolymers and the similar distributions of these relaxation times (*i.e.* similar segmental relaxation spectral shapes) observed in Figure 73, which again suggests that the local friction of the PI segments is comparable across all of the miktoarm copolymers. Additionally, the low molecular weight PS' block is estimated to have a $T_g > 350$ K.[327] As can be observed from Figure 77, the PI chain relaxation for the 18k(12k-3k')₂ copolymer is measured starting at 260K. At this temperature the PS' chains are effectively frozen within the cylindrical domain. In a study by Alig *et al.*, they show that in the linear triblock copolymer PS-PI-PS (with $M_{w, \text{PS, arm}} \sim 20 \text{ kg/mol}$), the PI chain relaxation is nearly indiscernible below the T_g of the PS block due to both of the PI chain ends being immobile at the interface with the glassy PS domains.[134] While some fluctuations of segments at the interface are expected, the length-scale of these fluctuations have been determined to be ~ 8 monomeric units, which is less than half of the degree-of-polymerization of the PS' blocks.[134] Therefore, we argue that any interphase fluctuations of the PS' segments would not contribute significantly to the end-to-end dynamics of the PI chains in the 18k(12k-3k')₂ copolymer, and the PS' block does not migrate into the PI domain at the measured temperatures and timescales.

To consider mechanism 1, we return to the SAXS profiles of the polymers with asymmetric PSPI_2 and $\text{PS}(\text{PI-PS}')_2$ architectures in Figures 64 and consider the decreased stretching energy of the PSPI_2 polymers in comparison with symmetric architectures, as described earlier. As determined from the SAXS analysis earlier, the PI chains terminated by the short PS' block in the $18\text{k}(12\text{k}-3\text{k}')_2$ copolymer are stretched within the PI domain compared to the $18\text{k}-10\text{k}_2$ system. In PS-PI-PS systems, PI chains that span the PI domain and are anchored at the interface with the PS block impart an elastic force (also considered as stretching energy) on the junction point.[126] In the $\text{PS}(\text{PI-PS}')_2$ polymer architecture, however, the elastic force of the two PI chains is distributed to a single PS chain at one end and individually to two separate PS' chains at the other end. For this molecular depiction of the $\text{PS}(\text{PI-PS}')_2$ architecture, the elastic force of the PI chains on the PS junction would be greater than that imposed to a single PS' junction. Therefore, with the PS' block determined to be immobile at experimental temperatures and timescales, and the argument for stretching energy of two PI chains dissipated by the single PS junction, we suggest that the dynamical origin of the PI chain relaxation in the $\text{PS}(\text{PI-PS}')_2$ polymer is in the fluctuations of the PI chain ends at the PS junction point.

In Figure 77b, the slow relaxation observed from $300\text{ K} < T < 360\text{ K}$ for the $18\text{k}(12\text{k}-3\text{k}')_2$ copolymer is normalized by the peak frequency and maximum value of the dielectric loss. This representation reveals that this relaxation narrows with increasing temperature. A narrower distribution of chain relaxation times with increasing temperature presumably corresponds to an evolution towards homogeneous chain conformations. The chain relaxation rates from the HN fits at each temperature data are displayed in Figure 80 and fit with the Vogel-Fulcher-Tammann (VFT) equation. The rates for the $18\text{k}(12\text{k}-3\text{k}')_2$ polymer are fit with an Arrhenius equation. The fit parameters for the VFT or Arrhenius equations for these data are found in Table 16. This Arrhenius-like temperature dependence is in contrast to the temperature dependence for ω_n in linear diblock copolymers and

all the other miktoarm copolymers in this study. The Arrhenius-like temperature dependence for the slow chain relaxation is uncharacteristic for block copolymer chain relaxations. It has been shown that a decrease in conformational entropy (S_c) for glass formers results in a reduction in cooperative motion.[328] This suggests that there is a reduction in the cooperativity of these chain dynamics within the domain of the $18k(12k-3k')_2$ polymer compared to other polymers. The single thermal activation energy barrier at experimental temperatures for chain dynamics in the $18k(12k-3k')_2$ copolymer is, therefore, due to a decrease in S_c .

In conjunction with the earlier discussion regarding PI chain stretching for the $PS(PI-PS')_2$ copolymer architecture and the relative increase in the elastic force on the junction point between the two PI chains and PS block compared to each individual PS-PI' junction, arises from a decrease in the topological degrees of freedom of PI segments (*i.e.* decreased S_c). We have also already discussed reductions in cooperative motions in terms of the requirement to maintain a uniform segment density (*i.e.* osmotic constraint). With this perspective, we conclude that the dynamics of the PI chain measured by BDS in the $18k(12k-3k')_2$ copolymer is due to fluctuations at the $PS-PI_2$ junction with a single activation energy of $\sim 28 \text{ kJ mol}^{-1}$.

Next the molecular weight dependence of the PI chain relaxations in these polymers will be discussed. The vertical line in Figure 80 corresponds to $T = 320\text{K}$. The rates at this temperature are plotted against PI arm molecular weight in Figure 81 where the molecular weight dependence of τ_n for these systems are compared with data from the literature.[46, 272, 329, 330] The prediction by Doi and Edwards for the relaxation times of normal modes of entangled flexible homopolymers is

$$\tau_p = \frac{\zeta N^3 b^4}{\pi^2 k_b T a^2 p^2} \quad 95$$

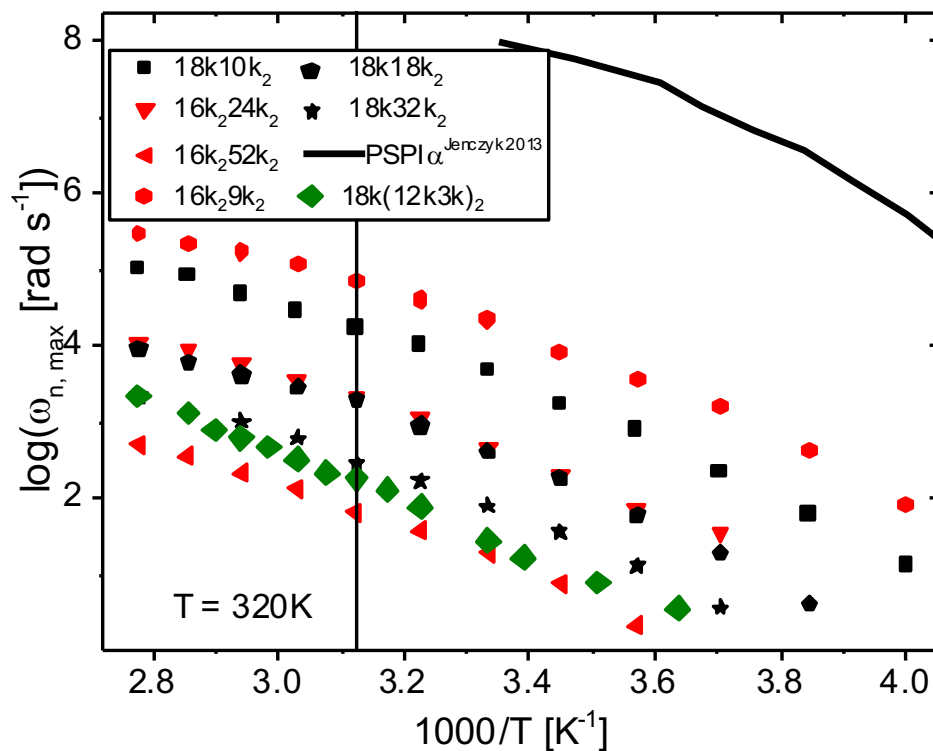


Figure 80: Normal mode relaxation rates plotted versus inverse temperature for all miktoarm polymers investigated. Segmental relaxation rates for PI in a lamellar forming PS-PI diblock copolymer from literature is included for reference (solid line).[119] These data were fitted with Vogel-Fulcher-Tammann equation and the resulting parameters are shown in Table 16 below.

Table 16: VFT or Arrhenius parameters to the PI chain relaxation rates for the miktoarm star copolymers

Sample	b	m (-E_a/R)	
18k(12k-3k') ₂	12.56	-3.31	
Sample	T₀	ω_∞	B
18k-10k ₂	156.5	2.61E+08	1570
18k-18k ₂	183.5	3.51E+06	1043
18k-32k ₂	168.0	2.90E+06	1379
16k ₂ -9k ₂	170.0	1.30E+08	1137
16k ₂ -24k ₂	151.0	3.83E+07	1668
16k ₂ -52k ₂	186.0	2.84E+05	1098

VFT eqn: $\log(\omega_n) = \log(\omega_\infty) + B(T-T_0)^{-1}$,

Arrhenius eqn: $\log(\omega_n) = b + m T^{-1}$

In Equation 95, ζ accounts for local friction, N is the number of segments in the polymer chain, b is the segment length, a is the Rouse tube diameter (accounting for entanglement of the chains), T is the absolute temperature, k_b is the Boltzmann constant and p is an integer corresponding to the eigenvalue of the chain relaxation mode.

The data in Figure 81 generally follow the experimental power law of $\tau_n \sim M_{w,PI}^{3.7}$ observed for entangled PI, which is slightly increased compared to Eqn. 95. This power law holds for tethered PI such as in phase-separated PS-*b*-PI linear diblock copolymers and PI star homopolymers, but with a 4-fold increase compared to free chains ($4\tau_n = \tau_{n,tethered}$).[43, 331]

For the PS₂PI₂ polymers, the power law and tethered Rouse chain predictions hold quantitatively. We note that because the spectral shapes of the chain relaxation for the PS₂PI₂ polymers in this study are quite different, it is not evident that the same normal modes are probed by BDS, and the constraints on chain motion are likely dissimilar among differing morphologies as is observed for linear PS-PI systems (symmetric architectures)[92]. On the other hand, the spectral shapes of the PI chain relaxation in the PSPI₂ systems are morphology and molecular weight independent (*cf.* Fig. 74).

The τ_n for PI in the PSPI₂ systems in Figure 81 are slightly increased compared with the τ_n from symmetric chain topologies. Also, there is a slightly reduced molecular weight power law dependence $\tau_{n,PSPI_2} \sim M_{w,PI}^{3.5}$, suggesting a shift toward more Rouse-like dynamics. To our knowledge, only one other study has reported the PI chain dielectric relaxation times of a PSPI₂ miktoarm star copolymer.[272] The chain relaxation time for the PSPI₂ polymer in the work by Floudas *et al.* at 320K is also plotted against PI arm molecular weight in Figure 81 and agrees with the Mw dependence for our PSPI₂ polymers. Additionally, the spectral shape of the chain relaxation for their PSPI₂ polymer (shown in Fig. 82) is observed to be similar to those in our measurements.

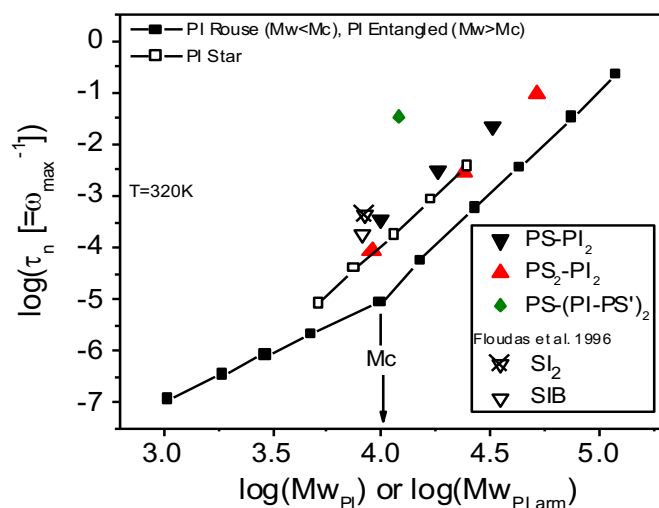


Figure 81: Mean PI chain relaxation times (τ_n) at 320K plotted versus PI arm molecular weight ($M_{w,PIarm}$) for all miktoarm copolymers studied with data for linear and star PI homopolymers from the literature[46, 49, 92, 138]. Additional PSPI₂ timescales are included from the study by Floudas *et. al* where “SI₂” is analogous to PSPI₂ and “SIB” has one polyisoprene block replaced by polybutadiene.[272]

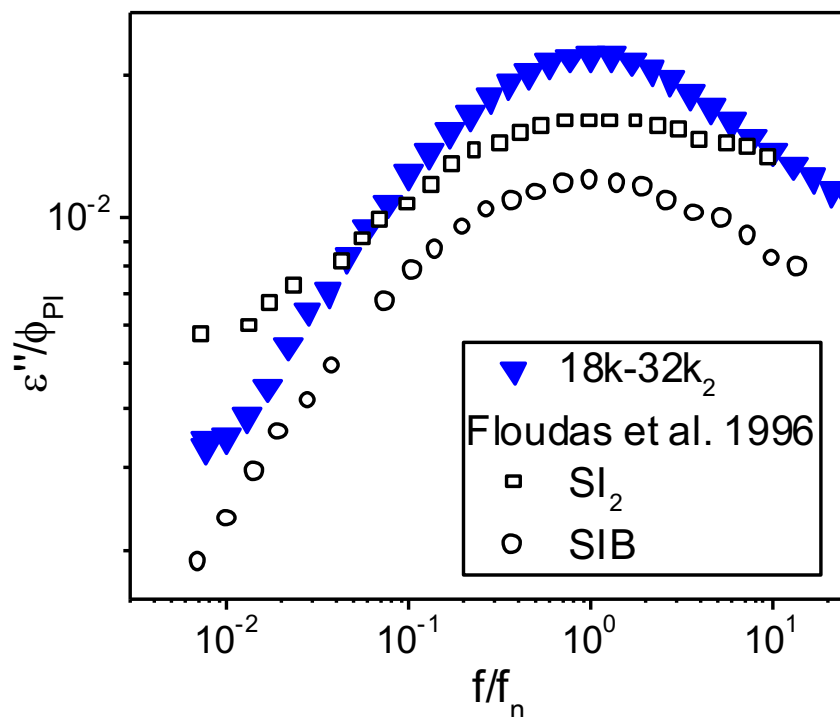


Figure 82: One other publication reports dielectric loss chain relaxation spectra of a miktoarm star copolymers of PSPI₂ architecture, where SI₂ is the same as our PSPI₂ architecture with Mw_{PS} = 7.6 kg/mol and Mw_{PI, arm} = 8 kg/mol and SIB has one PI arm replaced by polybutadiene.[272] Here the chain relaxation normalized by the PI volume fraction for our 18k-32k₂ polymer is compared against that for the similar PSPI₂ polymer, and a miktoarm star terpolymer with one arm of polystyrene, one arm of poly(cis-1,4-isoprene) and one arm of polybutadiene. The similarity in spectral shapes of this chain relaxation is in agreement with our data.

From Eqn. 94 and our arguments above regarding chain stretching and area per molecule at the interface, it is likely that the marginally slower chain relaxation times for the PSPI₂ polymers at a given molecular weight are most likely due to a slight average decrease in a (the diameter of the confining Rouse tube) due to decreased osmotic constraints on the chain relaxation which alleviate chain stretching as determined from our measurements and illustrated schematically in Figure 83.[200, 203, 332, 333]

Finally, the dynamic evidence of the effect of the asymmetric miktoarm star architecture is engrossed with the analysis of the dielectric strengths of the chain relaxations $\Delta\epsilon_n$ (analogous to $\Delta\epsilon$ in Eqn. 89) for the summed parallel dipole moment relaxation in Eqn. 90, are displayed in Figure 84 for all of the miktoarm star copolymers. These $\Delta\epsilon_n$ values are normalized by absolute temperature (T) and ϕ_{PI} for all of the miktoarm copolymers. For PI homopolymers, this normalized $\Delta\epsilon_n$ is constant with temperature above the critical molecular weight ($M_c \sim 5,000$ g/mol) and follow the dynamical description of the average chain relaxation by Gaussian statistics.[46, 69] Assuming monodisperse chains, the equation for dielectric strength of the chain relaxation is

$$\Delta\epsilon_n = \frac{4\pi N_a \mu_{||}^2}{3k_b T M_{w,PI}} F g \phi_{PI} \langle R^2 \rangle \quad 96$$

where N_a is Avogadro's number, $\mu_{||}$ is the parallel portion of monomeric dipole moment, k_b is Boltzmann's constant, $M_{w,PI}$ is the molecular weight of the PI arm, F is the Onsager factor that corrects for non-zero local electric field fluctuations due to polarization cross-correlations and is assumed to be unity for all Type-A polymers[49], g is the Kirkwood-Fröhlich correlation factor that considers cross-correlations in the local correlation function (as briefly mentioned with respect to Eqn 90), and ϕ_{PI} is the volume fraction of PI.

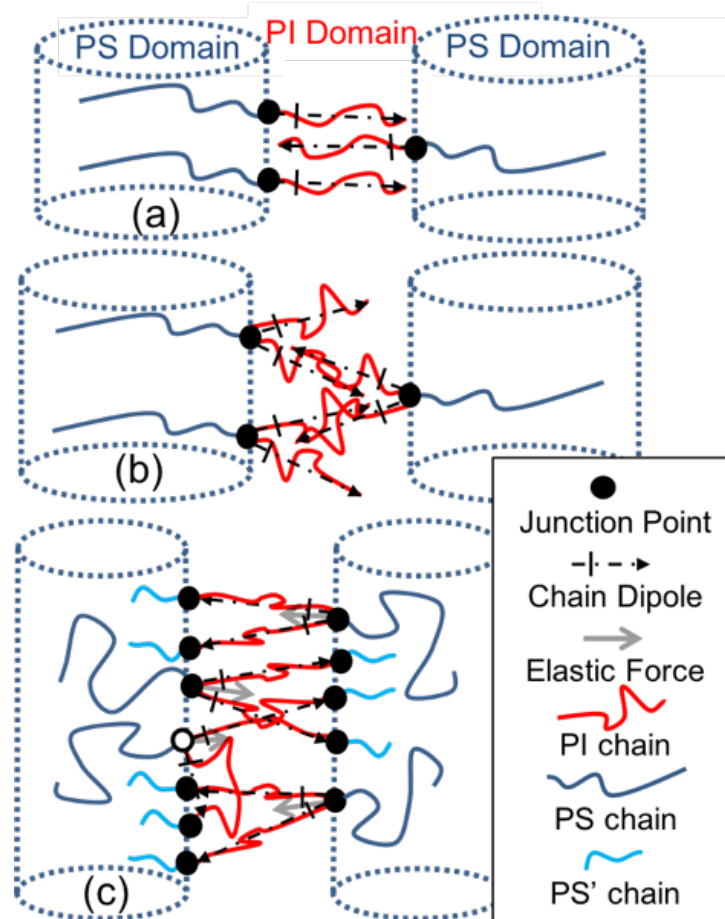


Figure 83: Schematic illustration showing chain stretching in phase separated linear PS-*b*-PI diblock copolymer (a), PSPI₂ miktoarm copolymer (b) and PS(PI-PS')₂ miktoarm copolymer (c). PS cylinder morphology is chosen for simplicity. The image depicts typical chain stretching normal to the interface for the PS-*b*-PI polymer, which we predict to be similar to that found in the PS₂PI₂ systems. The PSPI₂ system is shown to have decreased orientational anisotropy and reduced chain stretching. The PS(PI-PS')₂ is depicted as having PI chains spanning across the PI domain as bridges. The one PS(PI-PS')₂ polymer with an unfilled junction point symbol displays the PI chain bending back to form a loop. A relative increase in elastic force is depicted at the junction of the PS and PI chains in the PS(PI-PS')₂ polymer compared to other PS/PI junction points as discussed in the main text.

The $T\Delta\epsilon_n \phi_{PI}^{-1}$ in Figure 84 are nearly temperature independent for all PSPI₂ and PS₂PI₂ polymer. However, with changes in PI molecular weight, the values of $T\Delta\epsilon_{HN} \phi_{PI}^{-1}$ are constant for the PSPI₂ polymers but vary among the PS₂PI₂ polymers. The variations in $T\Delta\epsilon_{HN} \phi_{PI}^{-1}$ among the PS₂PI₂ samples in Figure 84 can be explained through another parameter that describes local constraints on chain conformation, the characteristic ratio ($C_\infty \sim \langle R^2 \rangle / M_{w,PI}$, which for PI homopolymer is 4.8)[334]. Assuming $g=1$ for the PSPI₂ and PS₂PI₂ polymers, rearranging Eqn. 96 shows that $T\Delta\epsilon_n \phi_{PI}^{-1} \sim C_\infty$.

The increase in PI molecular weight from the 16k₂-9k₂ copolymer to the 16k₂-24k₂ copolymer brings about a change from spherical PI morphology to lamellar morphology which is paired with a decrease in PI stretching energy due to the osmotic constraint. Consistent with this change in stretching energy, the estimate of the characteristic ratio, $C_\infty = \langle R^2 \rangle / N\mathbf{u}^2 \sim \langle R^2 \rangle / M_{w,PI}$, where N is the number of $\mathbf{u}$ bond vectors of PI, is decreased for the 16k₂-24k₂ copolymer compared to 16k₂-9k₂. These similar values of $T\Delta\epsilon_n \phi_{PI}^{-1} \sim C_\infty$ for the PSPI₂ polymers suggest that the relative constraints on PI chain segment to stretch away from the interface is relatively constant among differing morphology in this architecture. These trends further indicate that the effects of morphology on chain conformation are reduced for the PSPI₂ molecular architecture as compared to the PS₂PI₂ polymers.

Conversely, in Figure 84 the 18k(12k-3k')₂ polymer has an increased $T\Delta\epsilon_{HN} \phi_{PI}^{-1}$ compared to the other 3-arm miktoarm copolymers by a factor of ~ 2 with an empirical temperature dependence in T increasing at a slope of 1/3. This corresponds to an increase in C_∞ that further increases with temperature. To explain this, we refer to arguments made by Watanabe and coworkers on the effects of loops and bridges in PS-PI-PS triblock copolymers.[56, 136] To study these effects, researchers probed PS-PI-PS polymers with a symmetric dipole inversion of the PI midblock which allowed for a dielectrically observable chain relaxation even without any effectively-free PI chain ends.[56, 126]

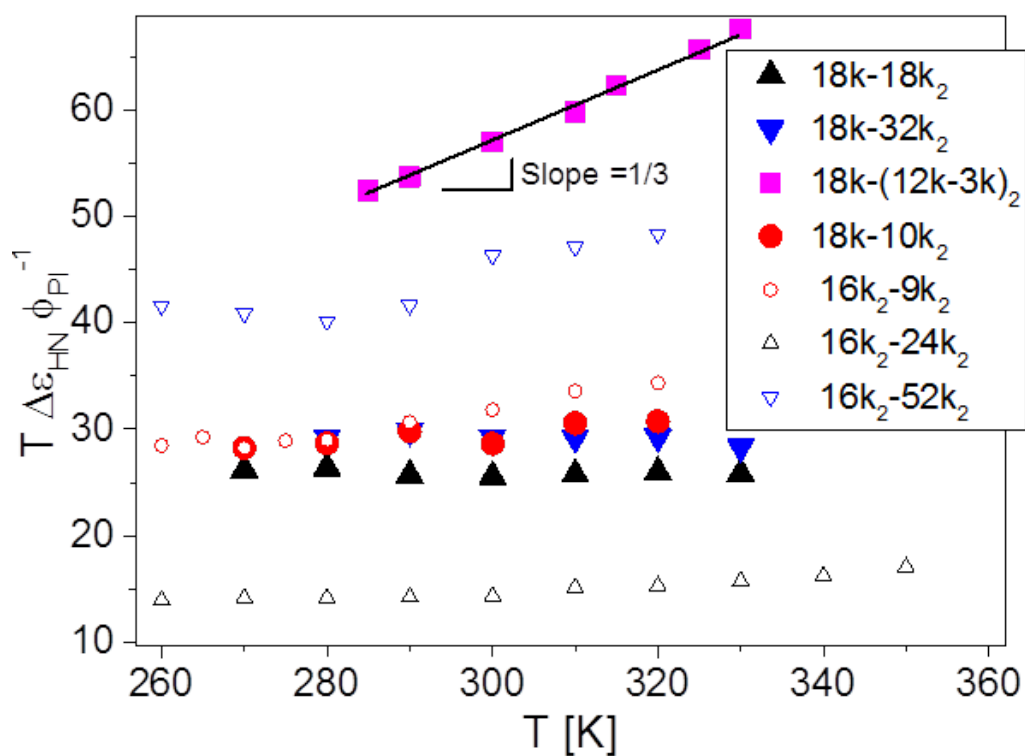


Figure 84: Normalized dielectric relaxation strength of the PI normal mode in miktoarm copolymers versus temperature. The solid line is a linear fit to the 18k(12k-3k')₂ data. The strengths are multiplied by PI volume fraction and temperature in order to represent the characteristic ratio, χ , of the PI chains as described by Eqn. 96.

The authors showed that the $\Delta\epsilon_n$ for PS-PI-PS with dipole inversion is greater by a factor of 1.5 compared to that for the linear diblock which has one free chain end.[126, 136] This was argued to occur because of cross-correlations in the local correlation function associated with PI chains that form knotted loops or bridges in the PS-PI-PS triblock spanning between PS domains, and, as these correlations increase and approach the case where all of the chains are knotted chains, the increase factor approaches 2.5 compared to the linear diblock.[69, 136]

In the PS(PI-PS')₂ polymer in this study, there is no dipole inversion within a single PI arm. However, we may consider the two individual chains of the PI block that are linked at the junction point with the PS block as a single probe chain with a dipole inversion at the domain interface. With this consideration, the junction point can be described as knotted loop in a PI chain with dipole inversion at the central point between the two PI-PS' junctions in the context of the model described by Watanabe and coworkers.[69, 136, 137] With the relatively larger elastic force at the PS interface toward the PI domain at the PS-PI₂ junction point, as described in Section 3, the motion of the PI chain between the two PS' blocks can be viewed analogously as a knotted loop. In addition to increased PI arm stiffness due to chain stretching across the interface (*i.e.* increased $\langle R^2 \rangle$), this higher normalized dielectric relaxation strength of the PS(PI-PS')₂ polymer at low temperatures is then qualitatively described by enhanced orientational polarization of PI chains by similar dynamics as knotted loops. Next, these dynamics will be discussed in terms of correlations of subchain motion to explain the slope of 1/3 observed in Figure 84 for the 18k(12k-3')₂ polymer.

In Figure 84, the normalized dielectric relaxation strength of PI chain for the PS(PI-PS')₂ polymer increases with temperature with a slope of 1/3. This linear increase has origins either through an increase in the average size of the PI chain end-to-end dipole (*i.e.* an increase in $\langle R^2 \rangle$ corresponding to an increase in chain stiffness) with increasing temperature or an increase in cross-correlations of bond vector motion, $\mathbf{u}(t)$, with increasing temperature. First, in conjunction with the

above discussion that determines no pull-out occurs for the $18k(12k-3k')_2$ polymer, we posit that it is unlikely that α would increase at $T < T_g$ of the PS and PS' blocks. Also, Figure 77 shows that the distribution in chain relaxation times decreases with increasing temperature which is contrary to an increased chain stretching with increasing temperature. Therefore, we will discuss the possibility of increased correlations in subchain motion through non-zero cross-terms among $\mathbf{u}(t)$ in the local correlation function $C(n, t; m)$ from Eqn. 90 as parameterized by g in Eqn. 96.

The Kirkwood correlation factor is defined as $g = 1 + \langle \cos \theta_{i,j} \rangle$ where $\theta_{i,j}$ is the angle of the dipole moment vector of the “ith” chain with respect to it's the “jth” nearest neighbor chain dipole vector.[49] For $g = 1$ there are no correlations in dipole orientation. For $g > 1$ the correlations in dipole orientation are more parallel. Finally, $0 < g < 1$ indicates that dipoles are oriented more antiparallel. In describing the Kirkwood-Fröhlich factor, g , Watanabe considers an additional initial orientational anisotropy (S_0) due to subchain tension after some strain, γ , for entangled chains. For incoherent subchains ($g = 1$) after some strain $S_0 = \gamma/3$, which describes the initial orientational anisotropy of non-entangled homopolymers. For coherent subchains using the model described by Doi and Edwards ($g = 4/5$) after some strain $S_0 = 4\gamma/15$ and therefore the orientational anisotropy of entangled homopolymers have a slight increase in anti-parallel orientations amongst chains ($0 < g < 1$ for antiparallel orientations). If we consider the subchain tension in entangled chains to be comparable to the stretching energy in block copolymers, it is logical that there would be a decrease in orientational anisotropy of subchains for the stretched chains of the $18k(12k-3k')_2$ polymer ($g = 1/3$) to have an anti-parallel orientation of neighboring chains. The increased chain stretching energy then corresponds to a decreased interfacial energy that allows for motion of the junction point between the PS block with the two PI chains in the $PS(PI-PS')_2$ polymer due to subchain tension during relaxation which places a non-zero force far from the chain ends.[64, 333]

Additionally, Watanabe showed that for the coherent motion of polymer subchains (*i.e.* cross-correlations of subchains at long times), the decreased g for entangled chains is due to a decrease in *initial* orientational anisotropy of subchains during the contour length fluctuation mechanism (also termed dynamic tube dilation).[137] In other words, there is enhanced motion near the chain ends compared to interior subchains which are confined by entanglements that create inhomogeneities in chain orientation during relaxation.[335] Furthermore, in lamellae forming PS-*b*-PI diblock systems, there is a direct correlation between an anti-parallel chain orientation across the domains and the chain end-to-end distances as the chains stretch away from the interface which are canceled out in dielectric measurements.[109, 144] In the PS(PI-PS')₂ polymer, we assert that PI chains are statically stretched between the PS domains. This decreases the orientational anisotropy at low temperatures compared to the PSPI₂ polymers. As the temperature increases, the elastic forces on the junction points required to maintain the interface decreases and releases subchain tension during relaxation toward equilibrium. This mechanism subsequently increases the contributions of knot-like dynamics, and corresponds to decreasing fraction of antiparallel chain orientations in the PS(PI-PS')₂ polymer which relax with increasing temperature.[88] Then, as the subchain tension is reduced with increasing temperature, there is a shift toward a more homogeneous distribution in chain relaxation rates with increasing temperature. This coincides with the analogous reduction in g for entangled homopolymer chains due to the non-zero subchain tension. Through these arguments, a positive slope in the temperature dependence of $T\Delta\epsilon_n\phi_{PI}^{-1}$ in Figure 84 for the PS(PI-PS')₂ polymer is rationalized through correlations in chain relaxation dynamics as parameterized by $g = 1/3$.

In summary, the architecturally asymmetric miktoarm star copolymer systems (PSPI₂) feature distributions in chain relaxation times and dielectric relaxation strengths that are not dependent on molecular weight or morphology, in stark contrast to the effects of morphological confinement observed for symmetric

diblock systems (PS-*b*-PI or PS₂PI₂). This contrast is argued to be due to a reduced energy of chain stretching. The segmental relaxations for all PI chains are observed to be comparable for all architectures and morphologies considered in this study. Finally, to strengthen the argument regarding chain stretching and dynamics, the PI chain relaxation was measured for the PS(PI-PS')₂ polymer. This chain relaxation is observed even with the two PI chains linked at both ends with the PS or PS' blocks and has an increased dielectric relaxation strength compared to other PI systems with an additional temperature dependence which we attribute to increased chain stretching and sub-chain cross-correlations with temperature.[182, 195]

Conclusions

Based on the results and arguments presented above, we conclude that in phase separated miktoarm star copolymer systems, topological asymmetry in the number of arms in each block gives rise to more uniform chain motion compared to block copolymers with symmetric molecular architecture. This was determined through investigation of the spectral shapes of the PI dielectric normal among different molecular weights, and therefore, morphologies in three PSPI₂ polymers, in contrast to the significant dynamical changes observed for symmetric PS₂PI₂ polymers and data for linear diblock PS-*b*-PI systems from the literature. Additionally, the chain relaxation times at 320K for various PI molecular weights in the PSPI₂ polymers are slightly increased compared to the τ_n for other tethered PI systems. This reveals that the architectural imbalance in the number of arms per block plays a role in altering the dynamics of polymer chains. Furthermore, a dielectric chain relaxation is observed for the PS(PI-PS')₂ miktoarm star copolymer where both PI chain ends are embedded in the glassy PS' domain. Compared to the practically undetectable PI dielectric chain relaxation in PS-PI-PS linear triblock copolymers, the dramatically slower PI chain dynamics are observed to exhibit a narrower relaxation time distribution, and have an increased, temperature-

dependent dielectric relaxation strength ($\Delta\epsilon_n$) compared to the other PI systems. We argue that the temperature dependence of $\Delta\epsilon_n$ results from an elastic force imbalance at the PI chain ends due to the tri-functional junction point of the PS block and two PI chains resulting in, in conjunction with analysis of the SAXS data. These contributions cause cross-correlations in chain motion as parameterized through the Kirkwood-Fröhlich factor (g). These results were discussed in terms of a subtle counterbalance between contributions from chain stretching and the thermodynamic requirements of phases separation in block copolymers. We demonstrate that subtle modifications to molecular architecture can have substantial impacts on the internal constraints on molecular dynamics that ultimately determine macroscopic physicochemical properties in polymeric systems.

Part I Conclusions

All of the studies in Chapters 4-6 combine aspects of phase separation with branching of chains from a central junction point. The dynamics of polyisoprene segments in the rubbery state for phase separated block copolymers when compared to homopolymer polyisoprene systems are known to be quite similar[91, 92, 207, 285, 336, 337]. The segmental relaxation that governs the dynamic glass transition, known as the dielectric α relaxation, is slightly slower in phase separated systems due to small differences in localized frictions that arise from phase separation with no appreciable effect from the molecular architecture in diblock systems. From the studies in Chapter 4, this is not so for the ABC miktoarm terpolymer. On the other hand, the global polymer relaxations were shown to deviate from those observed linear diblock under specific confinements based on the block copolymer architecture. This is shown by comparison to the linear diblock systems through three specific experimental investigations: 1) The effect of molecular architecture on dynamics in the ABC miktoarm star terpolymer, 2) The effect of architecture in lamellae forming miktoarm star copolymers with the 4-arm PS_2PI_2 and 3-arm PSPI_2 architectures, and 3) The effect of morphology and molecular weight in the asymmetric architecture of the 3-arm PSPI_2 miktoarm star.

Chapter 3 shows through a meta-analysis of the PI dielectric chain relaxation that the spectral shape is morphology dependent. Also, the relaxation of the PI chain is dependent on the glassy or rubbery state of the counter block and on the order disorder transition. In Chapter 4, for PI in the linear diblock copolymers with a P2VP block, the dynamics of the PI chains are found to be consistent with the dynamics from the literature for the PS-PI systems. This is determined by deconvoluting the P2VP β -relaxations from the PI chain relaxations at similar temperatures and timescales by analytical procedures and by limited experimental methods. The analytical approach to deconvolution of the P2VP β -relaxation and PI chain relaxations was achieved for only one of the miktoarm star

terpolymers in the PS-PI-P2VP miktoarm star terpolymers, with the PI chain relaxation being similar to those observed for PI in other block copolymer systems.

In Chapter 5, the dynamics in lamellae block copolymer systems revealed that the dielectric chain relaxation shape is architecture dependent. There is an increase in the PI chain relaxation intensity relative to the volume fraction of the PI block compared to the architecturally symmetric linear system and 4-arm miktoarm system. This change in polarization relaxation of the PI chain is attributed to decreased anisotropy in chain motion that result from an increase area per junction point for the asymmetrical architecture as calculated from small angle x-ray scattering measurements. With respect to the dynamic models for polymer chains, the available states of chain conformations decrease near the interface due to decreased free volume but results in reduced stretching required for phase separation. In all the dynamical consequence of molecular architecture in the lamellae is more a function of architectural asymmetry than the functionality of the junction, and the more chains of one type allows the dynamics of those chains to become more isotropic. These results will be useful in rational design of thermoplastic materials, whose dynamical properties are governed by the entropy of the polymer chains.

Finally, in Chapter 6, the asymmetric miktoarm architecture is shown to give rise to a measurable chain relaxation when both PI chain ends are tethered to the glassy PS interface. This furthers the conclusion of the imbalance of architecture enhances the mobility of the junction of the blocks at the interface. Furthermore, the slightly slowed chain relaxation for similar molecular weights shows that, in the context of the tube model for the Gaussian chain, the confinements of the tube are decreased across various morphologies in the asymmetric architecture.

PART II: Nanoporous Silica Membranes

Introduction

The dynamic phenomena and physical properties of molecules under confinement are known to deviate from the bulk material. Part I of this dissertation focused on confinement with respect to the thermodynamic phase separated block copolymers and the effect of branching and non-linear architectures. In Part II, the dynamics of polymer systems confined within inorganic silica nanochannels or nanopores are investigated. One of the largest considerations for dynamics within nanoporous media is the change in the dynamic glass transition for different pore sizes and surface chemistries. Industrially, the effect of various levels of this type of confinement on material properties are becoming increasingly important as the electronic and medical devices become smaller and smaller. Additionally, the sensing of biomolecules, such as proteins or DNA, relies heavily on nanoporous media and understanding how these molecules move in nanochannels is very important.[338, 339]

The level of confinement within nanoporous media is often associated with the comparative diameter of the pore with the lengthscale of the polymer molecule for the particular phenomena under investigation. For example, as the diameter of the pore approaches the lengthscale associated with the cooperative motions of the dynamic glass transition (ξ , see Chapter 1 for details), the flow properties that are governed by these dynamics become altered[340]. On the other hand, dynamics at larger length-scales like that of viscoelasticity and entanglement (average end-to-end distance $\langle R^2 \rangle$ or radius of gyration R_g) are likely to become altered prior to that of the glass transition due to the larger molecule size associated with these dynamics. Furthermore, the effects of surface interactions, while negligible in the bulk state, account for an increasing fraction of the interactions of the system as the confinement increases. These surface interactions may either non-covalently bind or repel the polymer and thus hinder or enhance the motions. Finally, the conformational changes associated with

polymer chains must change from the bulk state in order to fill the space available in the pore.

For dynamics, a one dimensional (1D) confined system is considered for thin films, then a 2D confinement is achieved for materials within hard cylinders[147, 341-345]. Thin layer materials have shown that new dielectric relaxations are observed and that there is an increase in the distribution of relaxation times as the degree of confinement increases (*i.e.* film thickness decreases).[148, 149, 154, 346] For Type-A polymers like homopolymer poly(*cis*-1,4-isoprene) (PI), the new relaxation exists at timescales between the segmental and chain relaxations and is considered a sub-chain relaxation.[221, 330] These sub-chain relaxations are thought to occur due to segmental units adhering to the planar substrate surface causing intermediate polarizations of portions of the chain to contribute to the dielectric relaxation rather than the full end-to-end chain relaxation. These sub-chain modes have not been specifically identified for Type-A polymers in nanopore confined samples, but various confinement dynamics for these types of polymers have been measured as summarized below.

Types of Nanopores and Their Known Effects on Dynamics

There are several types of nanoporous media that are industrially and academically relevant to molecular confinements. Ceramic materials are often employed for their 3D porous networks, whereas silicon and aluminum substrates are used for formation of unidirectional pores. Because Part II focuses on materials in unidirectional silica pores, mesoporous materials will not be covered here. Therefore, the differences between the unidirectional pores of aluminum/alumina and silicon/silica are discussed below. Due to their surface chemistries aluminum and silicon form an anodic oxide layer that can be etched away electrochemically with an acidic electrolyte. The primary differences between the cylindrical channels that can be produced are the pore sizes and size distributions and arrangement of the pores within the substrate. Alumina nanopores are typically produced with a

phosphoric acid electrolyte to form regularly spaced pores in a hexagonal pattern through the aluminum membrane then relatively homogeneous pore sizes are controlled by different oxidation parameters. The regular order of these nanopores are of particular interest in industrial applications, and similar to silica, the surfaces of these pores can be modified by chemical reactions with the native -OH bonds (aluminum oxide) on the pore surface. By comparison to silica, the sizes of these anodized aluminum oxide (AAO) pores are larger approaching 20nm diameters whereas nanopores in silica can approach 1nm in diameter. Due to their commercial availability and safety considerations during processing, these types of pores are more widely used for academic investigations of confinement dynamics. Silica pores, however, require hydrofluoric acid electrolytes which adds an increased risk during preparation and limits industrial availability making the use of these types of pores much less popular [347, 348].

Both pore types have been used as nanoreactor conditions for free radical polymerizations with reaction kinetics that are different from bulk and revealing changes in material properties from bulk[349, 350]. For example, polymerization of vinyl ionic liquids monomers for ion transport in polymeric materials have only been performed in AAO nanopores with promising results for fast transport in solid substrates, but these materials have not been produced within silica pores [351, 352]. When traditional (non-polymeric) ionic liquid materials are infiltrated into these smaller pores the results show a change in temperature dependence of dc ionic conductivity for higher diffusion coefficients especially at low temperatures [353]. Thus, for materials in silica based nanopores, the degree of confinement is increased compared to AAO due to the smaller possible pore diameters. This increased confinement, for Type A polymers in silica nanopores showed an interfacial chain relaxation and faster relaxation times [354]. Additionally, the packing of molecules are changed from the bulk state resulting in decreased molecular densities [220]. For Type-A polymers investigated at in AAO pores, the dynamics are altered similarly as in the smaller pores, with breadths of relaxations

being increased with effects that are less pronounced particularly for lower molecular weights [355-357]. Also, chemical surface modification of AAO and silica substrates are performed by similar methods to react the native oxide layer with various silane chemistries. Results from these studies have shown that hydrogen bonding and other attractive or even repulsive surface interactions can alter the dynamics of materials and even increase ion transport properties[354, 358]. The studies in the following chapters progress the understanding of extreme nonconformant in of Type-A polymers and polymerized ionic liquids silica nanopores.

Outline

Part II contains two chapters that investigate polymeric materials under confinement within 6.5-7.5nm nanoporous silica membranes. Chapter 7 covers the chain and segmental dynamics of low molecular weight PI in nanopores as the radius gyration of the polymer approaches the pore diameter. Then, Chapter 8 shows the effects of *in-situ* polymerized monomeric ionic liquids within the pores. Additional data is collected for pores having different surface chemistries and how this affects the ionic conductivity of the resulting confined material. While these studies stand alone, they contribute results that fills the gaps in experimental knowledge for material confined in nanoporous media.

Chapter 7: Chain Dynamics as the Polymer Size Approaches the Pore Radius

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Kinsey, T., et al., *Elucidating the impact of extreme nanoscale confinement on segmental and chain dynamics of unentangled poly(cis-1,4-isoprene)*. Eur Phys J E Soft Matter, 2019. **42**(10): p. 137.

The polymer materials for this study were synthesized at the CNMS by YH with guidance from KH. The nanoporous membranes were prepared by TC or TK with instruction from CI. BDS measurements were made in bulk by TC and under confinement by TK. The manuscript was written primarily by TK with guidance, edits and suggestions from TC, YW and JC. JC provided the funding for this project.

Abstract

Broadband dielectric spectroscopy is employed to probe dynamics in low molecular weight poly (*cis*-1,4-isoprene) (PI) confined in unidirectional silica nanopores with mean pore diameter, D , of 6.5 nm. Three molecular weights of PI (3, 7 and 10 kg/mol) were chosen such that the ratio of D to the polymer radius of gyration, R_g , is varied from 3.4, 2.3 to 1.9, respectively. It is found that the mean segmental relaxation rate remains bulk-like but an additional process arises at lower frequencies with increasing molecular weight (decreasing D/R_g). In contrast, the mean relaxation rates of the end-to-end dipole vector corresponding to chain dynamics are found to be slightly slower than that in the bulk for the systems approaching $D/R_g \sim 2$, but faster than the bulk for the polymer with the largest

molecular weight. Analysis of the spectral shapes of the chain relaxation suggests that the resulting dynamics of the 10 kg/mol PI confined at the length-scales close to that of the R_g are due to non-ideal chain conformations under confinement decreasing the chain relaxation times. These faster chain dynamics of polymers under extreme geometrical confinement are necessary in designing nano-devices that contain polymeric materials within substrates approaching the molecular scale.

Introduction

The design of nanostructured polymer-based devices – such as photoresists, batteries, sensors for smart drug delivery, organic electronics gadgets etc. – requires detailed understanding of the interplay between decreasing product size, geometrical restriction, and polymer dynamics. Mechanisms associated with local polymer dynamics such as chain interpenetration, adsorption, configuration and conformation, all of which determine macroscopic material properties, are known to be influenced by spatial confinement[359-364]. For example, conformations of polymer chains in the bulk phase can be quantitatively described in terms of the radius of gyration (R_g). However, in the vicinity of solid surfaces, the conformations of the polymer chains are altered in a myriad of ways affecting the stiffness of the chain, free space for random motion of segments, etc., due to the nature of the interactions with the solid surface and the timescales of these interactions. These interactions lead to changes in its dynamics and resultant physical properties compared to the corresponding bulk system[341, 365-367]. For the case of confined polymers in nanoporous media, the length- and time-scales of these interactions can be investigated by varying the diameter of the pores and/or increasing the size (molecular weight) of the macromolecules. Some of the polymers whose dynamics have been investigated under confinement in nanopores include poly(2-vinylpyridine)[368], poly(dimethyl siloxane) (PDMS)[369, 370], poly(methylphenyl siloxane)[369, 371, 372],

poly(ethylene-alt-propylene)[373], poly(ethylene glycol)[374], poly(propylene glycol) (PPG)[354, 355, 364, 370, 375-377], and poly(*cis*-1,4-isoprene) (PI)[154, 357, 378].

A particular subset of dielectrically active *Type A* polymers[379] (such as PPG and PI) present an ideal model to study the segmental and chain dynamics due to the nonzero components of the dipole moment perpendicular and parallel to the chain contours, respectively. Thus, two dielectrically active relaxations at completely different time-scales can be studied by broadband dielectric spectroscopy (BDS). For these systems, BDS provides insight into the effect of confinement on both local and global dynamics which are critical for determining polymeric properties such as the glass transition and viscoelasticity, all of which are altered when the polymer is placed under confinement.

The majority of investigations of confined polymers have focused on thin films deposited on inorganic substrates for confinement in one dimension or infiltrated into nanoporous media for two-dimensional confinement. Previous studies of the *Type A* PI in nanopores have employed either controlled porous glass (CPG)[378] or anodized aluminum oxide (AAO) membranes[154, 357]. The latter system has the advantage of a narrow distribution of pore diameters. However, the chemistry of these membranes limits the smallest obtainable pore diameter to about 20 nm, and restricts the extent of possible confinement to that of several molecules[380]. In their study of PI confined in CPG, Petychakis *et al.*[378] showed that, depending on the size of the chain relative to pore radius, the normal mode was broadened due to topological constraints imposed on the chain. In a similar work, using self-ordered AAO pores, Alexandris *et al.*[357] demonstrated that a broadened distribution of relaxation times for the PI chain motion occurs even for pore sizes that are 50 times larger than the unperturbed chain dimensions, and argued that at such (low) levels of confinement, chain adsorption plays a more significant role than confinement itself. Related studies, such as the neutron spin echo study of PDMS by Krutyeva *et al.* or the pulsed field

gradient NMR study of PPG by Schönhals *et al.*, suggest that a two-layer model consisting of an adsorbed layer at the pore wall and a bulk layer is over-simplified and suggest a dynamical or interphase layer where timescales of the interactions of adsorbed and bulk-like chains cause a gradual slowing in the molecular motions of chains within the nanopores compared to bulk[363, 364]. Generally, these studies observed changes in the dynamics due to surface interactions, but the length-scales of the confinement rarely approached that of the R_g of the confined polymer chain. Therefore, the extent of the effect of geometrical confinement on the underlying relaxation dynamics of polymer segments and chains remains unresolved.

In the present work, we infiltrate unidirectional silica pores with mean diameter (D) of 6.5 nm with PI and systematically vary the molecular weight of the polymer so that, for the longest chains studied, $D \approx 1.9 R_g$. To this end, the aim is to increase the extent of confinement such that no bulk like layer presumably exists, and a high probability that all polymer chains interact with the pore surface, or at least some interphase layer where the molecules “feel” the effects of the confined chains, is achieved. To the best of our knowledge, this level of confinement for PI has not been previously reported. These results show changes in the spectral shapes and timescales of the chain relaxation when the radius of gyration (R_g) of the polymer becomes comparable to the length-scale of the nanopore. We show that drastic changes to the chain dynamics occur at these extreme levels of confinement, and attribute these changes to the non-ideal conformations that the polymer chains are forced to assume because of geometrical constraints.

Materials and Methods

Three polyisoprene (PI) polymers = 3.5 (PDI = 1.05), = 7.4 (PDI = 1.08), and = 10.3 (PDI = 1.09) kg/mol, termed 3k, 7k and 10k, respectively] having narrow molecular weight distributions were synthesized using anionic polymerization techniques under high-vacuum conditions (10^{-6} mmHg) in a glass apparatus

equipped with break-seals. All reagents were purified according to reported procedures[261]. The polymerization was carried out in benzene at 25 °C and sec-butyllithium was employed as the initiator and degassed methanol was used as the terminator. The material was precipitated in nonsolvent and washed several times. The resulting polymer was characterized by size exclusion chromatography (SEC) equipped with refractive index and light scattering detectors. ^1H NMR and ^{13}C NMR spectra were used to confirm the microstructures of the PIs. Dielectric experiments were performed on a Novocontrol High Resolution Alpha Analyzer equipped with a Quatro system with the capability of controlling temperature to a precision of 0.1 K under dry nitrogen atmosphere. Bulk dielectric measurements were made by applying 1.5V across a parallel plate capacitor prepared by sandwiching the polymer between two 15mm diameter brass electrodes with two 100 μm silica rod spacers to maintain sample thickness. The frequencies of the applied alternating electric field and temperatures ranged from 10^{-1} - 10^7 Hz and 200-320K at 5K intervals, respectively. The same applied potential, frequency range and temperatures employed for bulk systems were used for dielectric measurements of PI in pores.

The silica nanopores were prepared by wet electrochemical etching of a highly doped <100> oriented silicon wafer in a home-built set-up. The resulting silicon pores were washed several times with reverse osmosis milliQ water, then oxidized by heating in a furnace at 700°C for 5 hours, then 880°C for 6 hours. Under these preparatory conditions, previous characterization work using NMR-cryoporometry and scanning electron microscopy (SEM) shows that unidirectional, 6.5 nm diameter porous silica membranes with a porosity of 7% are obtained²¹⁻²³. The membranes were dried to remove any excess adsorbed moisture by heating to 250°C under 10^{-8} mbar oil-free vacuum for 24 hours before infiltrating the polymers.

Polymers were infiltrated into nanoporous silica membranes by coating both surfaces of the membrane then pulling a 10^{-8} mbar vacuum and heating to 60 °C

for 40-48 hours. Then, immediately upon cooling to room temperature and removal from the vacuum, excess material on the surface of the pores was removed using Kimwipes and lens paper, then subsequently sheared multiple times between clean glass slides until no residual polymer was transferred from the membranes to the slides. Then the parallel plate capacitor was prepared for dielectric measurements by placing 6 mm diameter, 750 nm thick aluminum foil disks concentrically to each side of the membrane to ensure proper electrical contact with the two 6 mm brass electrodes. The confined polymer was then immediately measured over the temperature range above. This filling and measurement procedure was rigorously followed to ensure the equilibration dynamics (that have been reported to occur at much longer timescales than that of the polymer chain dynamics and viscoelastic flow) for each of the different PI samples under confinement are held constant throughout this study[344]. In that way, only the effects of the polymer confinement on chain dynamics as a function of the M_w of the PI are probed. By maintaining a constant pore diameter, the relative amount of polymer segments in contact with the pore surface is constant across each sample, and thus the kinetics of surface adsorption and equilibrium dynamics are not considered[343].

As a final note, there are deviations in pore filling procedure from the literature that fall into two categories: coating both surfaces of the membrane with polymer or only one surface. To test these two methods, the 7k PI was filled both ways then measured with BDS. In Figure 85, the temperature dependent dielectric loss data on both heating and cooling from 180K-400K at both $\sim 10^4$ Hz and $\sim 10^0$ Hz are shown for 7k PI infiltrated in the pores by wetting both surfaces of the membrane (in black) and wetting one surface of the membrane (in blue). If inclusions of air were to be trapped in the pore by PI filling in both directions, the resulting dynamics would be expected to differ from pore filling of PI from one direction. This however was not the case and heating and cooling curves are reproducible.

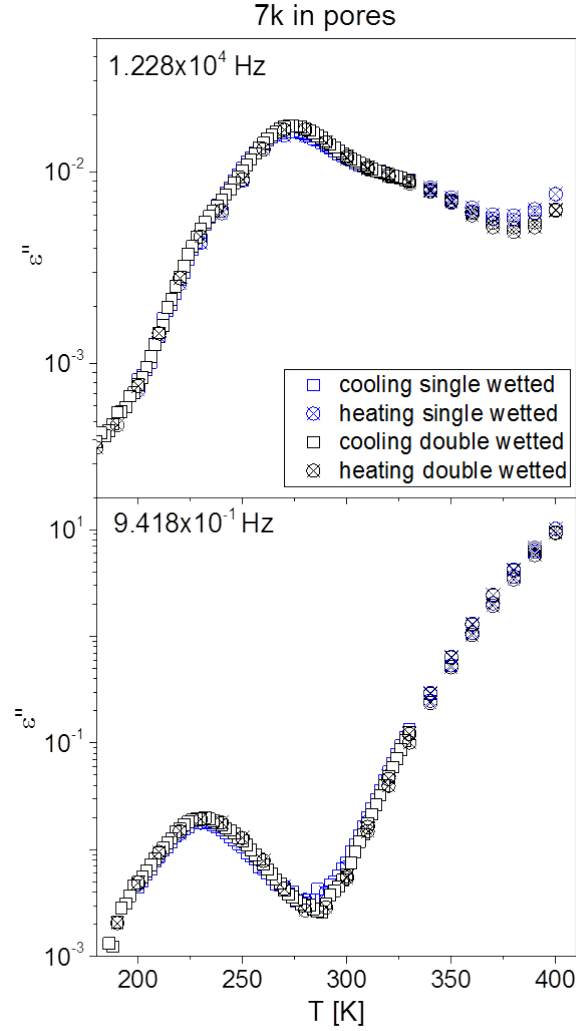


Figure 85: Dielectric loss vs temperature at two representative frequencies (1.228×10^4 Hz top and 9.418×10^{-1} Hz bottom) for the 7k PI in pores after using the filling procedure described in the main text by both wetting both sides of the pores with PI (black symbols) and wetting only a single side of the pores with PI (blue) before pulling vacuum. Additionally heating and cooling curves (crossed circles and open squares, respectively) are shown to be the same for either wetting procedure, and indicate the dynamics measured in this study are independent of the filling procedure.

Results and Discussion

The dielectric loss (ϵ'') corresponds to energy from the electric field lost by dipolar relaxation. The ϵ'' spectra for all polymers in bulk and under confinement are displayed in Figure 86 at selected temperatures. The spectra for bulk PI are displayed in open symbols and show two distinct dielectric relaxations. First, a higher-frequency process is observed at lower temperatures, and corresponds to the segmental relaxations[49]. The spectral shape corresponding to the segmental relaxation is not altered under confinement; however, the rates of maximum loss for this relaxation peak are faster at corresponding temperatures. Second, a slower relaxation in bulk corresponding to the end-to-end dipole vector of the chain is observed at higher temperatures. This relaxation decreases in rate with increasing molecular weight[89]. In contrast to the modest effect of confinement on the segmental relaxation, the chain dynamics are significantly altered for each polymer within the 6.5nm pores. This polymer is known to have a higher-frequency β relaxation wing attributed to libration motions at local length-scales which is observed in bulk at the lowest temperatures[381]. These β relaxations are too weak to be observed under confinement and are therefore not investigated further.

A significantly broad relaxation dominates the spectra at intermediate timescales for all polymers within 6.5nm pores (see dotted fit lines in Fig. 86), with the segmental relaxation only observed as a high frequency wing at low temperatures (see dash-dotted fit lines in Fig. 86). At high temperatures, a low frequency shoulder is observed emerging from this dominant, intermediate relaxation. This low frequency shoulder is barely visible for the confined 3k PI and becomes more prominent with increasing molecular weight (see dashed fit lines in Fig. 86). To be consistent with previous reports in the literature of confinement-induced relaxations, we will term the intermediate relaxation the confined chain relaxation, or CCR[330].

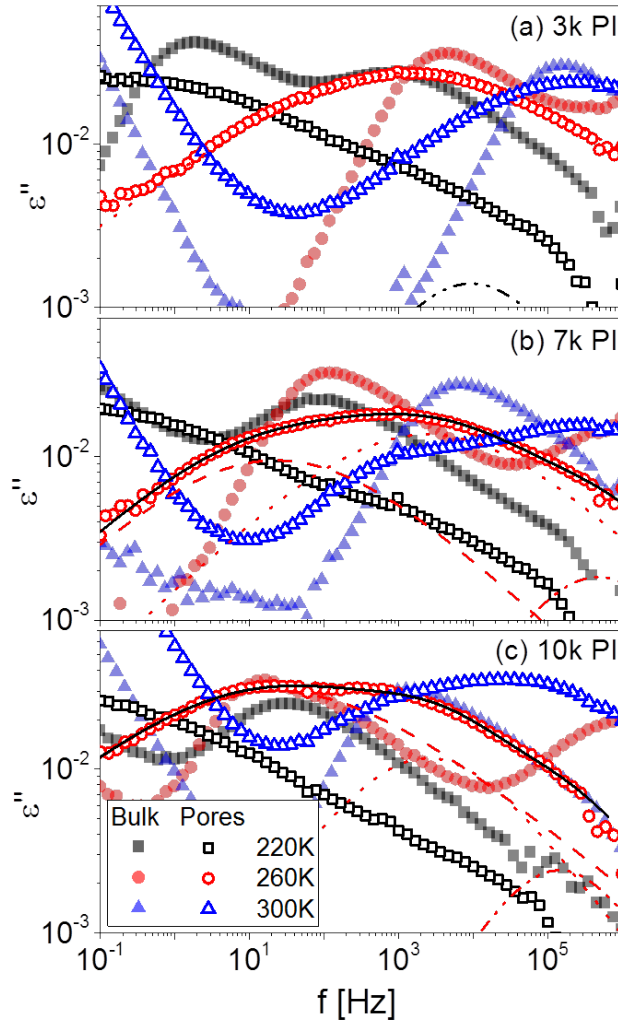


Figure 86: Isothermal dielectric loss spectra at selected temperatures for the 3k (a), 7k (b) and 10k (c) polymers in bulk (closed symbols) and in pores (open symbols). Fit lines from Eqn. 97 are included for the segmental relaxation (dash dot), CCR (dotted) and slow relaxation (dashed) at 260K, as well as a linear combination of all fits (solid lines). The segmental relaxation is outside the measurement window for the 3k PI in pores, therefore, the fit for this relaxation is shown for 220K instead.

The shape of this CCR is well described by the empirical Cole-Cole function (Eqn. 97) for the 3k PI. The Cole-Cole function for the dielectric loss is given by:

$$\varepsilon^* - \varepsilon_{\infty} = \frac{\Delta\varepsilon}{1+(i\omega\tau)^{\alpha}} \quad 97$$

where ε^* is the complex dielectric function, ε_{∞} is the high frequency limit of the real part of ε^* , $\Delta\varepsilon$ is the dielectric relaxation strength, ω is the angular frequency of the applied field, τ is the relaxation time, and α is the shape parameter. For the 7k and 10k PI a linear combination two Cole-Cole functions is required for the additional low frequency process that emerges with increasing molecular weight. We will term this low frequency process the slow chain mode or slow relaxation. A possible consideration of this low frequency process that emerges with increasing M_w of PI under confinement is that a recently described chromatographic phenomena of M_w is occurring during imbibition of polymers into pores[382]. It was observed that the capillary filling of smaller polymer chains into pores occurs faster than larger ones. If this were the case, we may expect a skewed distribution of PI chain relaxations toward low frequencies. However, the bimodal distribution of the PI chain relaxations (we term the CCR and slow relaxation) is not explained by this phenomenon. Additionally, the extremely low PDIs of the PI in this study exclude overlap of molecular weights present in each of the samples used in this study. Therefore, this slow chain mode is due to different effects of confinement on the various molecular weights of PI in the 6.5nm pores.

Another possibility is that this relaxation is a polarization process of some interface within the pores, *i.e.* Maxwell Wagner Sillars (MWS) polarization. The main possibility for this type of polarization would be air pockets that were not fully evacuated during filling of PI into the nanopore at elevated temperature and lowered pressure. To test this possibility the relaxation time (τ) of such a polarization process was estimated using

$$\tau = \varepsilon_0 \left[\frac{(1-n)\varepsilon_m + n\varepsilon_f + n(\varepsilon_m - \varepsilon_f)\phi_f}{(1-n)\sigma_m + n\sigma_f + n(\sigma_m - \sigma_f)\phi_f} \right] \quad 98$$

where ε_0 is the permittivity of free space ($8.854 \times 10^{-12} \text{ C}^2\text{N}^{-1}\text{m}^{-2}$), n is the shape parameter of the pockets ($1/3$ for spheroids, $1/2$ for rods), ϕ_f is the volume fraction of the filler, and the subscripts “f” and “m” correspond to the filler and matrix, respectively, with ε as the static permittivity, and σ is the dc conductivity for the corresponding phases. In this case study, air is the filler in a polyisoprene matrix. The room-temperature static permittivity of polyisoprene is 2.7 with a dc conductivity of $1 \times 10^{-9} \text{ S m}^{-1}$. [49] The static permittivity of air is 1 with a DC conductivity of $1 \times 10^{-12} \text{ S m}^{-1}$. Relaxation times at room temperature vs shape parameter for MWS polarization of air pockets in polyisoprene are plotted at various volume fractions in Figure 87. The measured relaxation times at room temperature reported in our manuscript are in the range of $4.5 \times 10^{-7} \text{ s}$ to $2.12 \times 10^{-4} \text{ s}$. The MWS relaxation times (τ_{MWS}) found in Figure 87 are at least two orders of magnitude slower than the PI in nanopores are reported later. Similarly, Figures 87a and 87b are for air pockets in a silica matrix ($\varepsilon=3.8$, $\sigma=1 \times 10^{-19}$) and PI pockets in a silica matrix, respectively (note $n=0.5$ is for rods, and a volume fraction of 7% is included for PI in silica). All possibilities for these types of MWS polarizations are too slow to be considered as an explanation for the relaxations we report. Therefore, experimental evidence that air inclusions, if any exists, have negligible impact on the main results reported in this article.

Next the the dielectric loss spectra at $T = 280 \text{ K}$ normalized by the average rate ($\omega_{\text{CCR max}}$) and dielectric strength of the CCR Cole-Cole fit ($\Delta\varepsilon_{\text{CCR}}$) are displayed in Figure 88. A low frequency shoulder clearly emerges with increasing molecular weight. This slow relaxation is possibly present for the confined 3k PI, but it is too weak to be accurately fit along with the CCR. The shape parameter, α , in the Cole-Cole fit function for the CCR increases slightly with increasing molecular weight and decreases with decreasing temperature (see Fig. 89a).

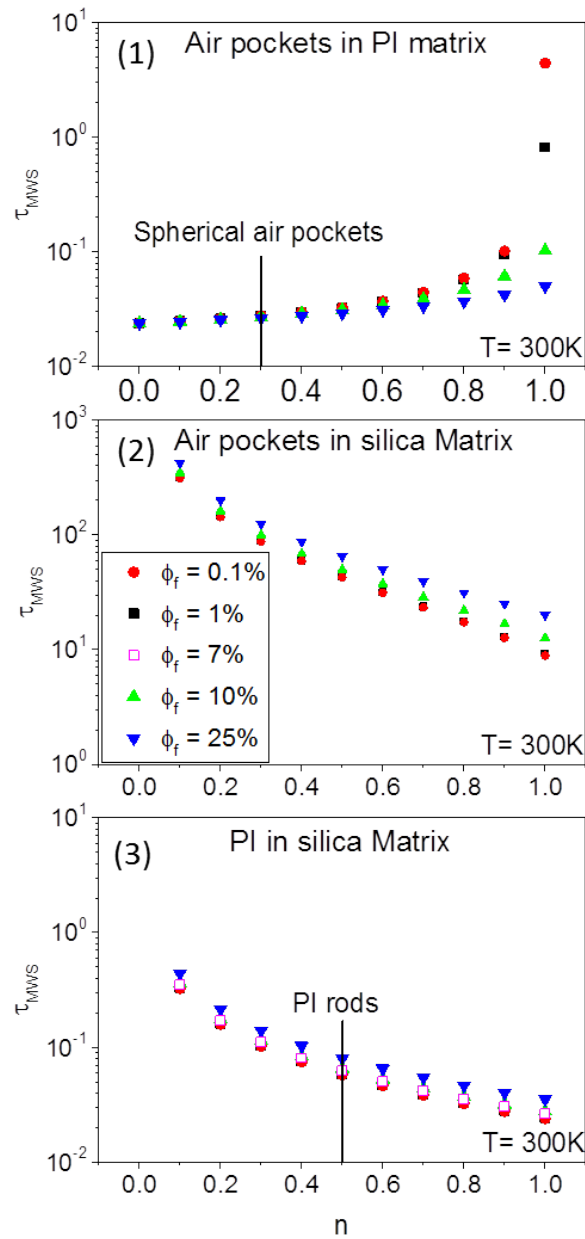


Figure 87: MWS polarization relaxation times vs shape parameter for various volume fractions of inclusions of air pockets in a PI matrix (1), air pockets in a silica matrix (2), and PI in a silica matrix (3).

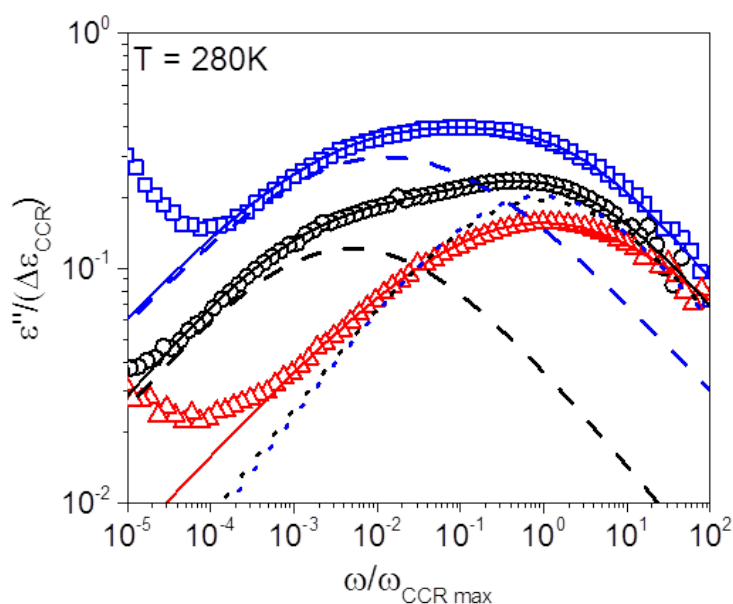


Figure 88: Dielectric loss normalized by the dielectric relaxation strength and mean relaxation rate of the CCR for 3k (triangles), 7k (circles) and 10k squares within 6.5nm pores. The fit lines from Eqn. 97 are shown for the CCR (dotted) and the slow relaxation (dashed) and the summation of all fits (solid). The 3k PI, having no fit for the slow relaxation only displays the CCR relaxation fit (red solid line).

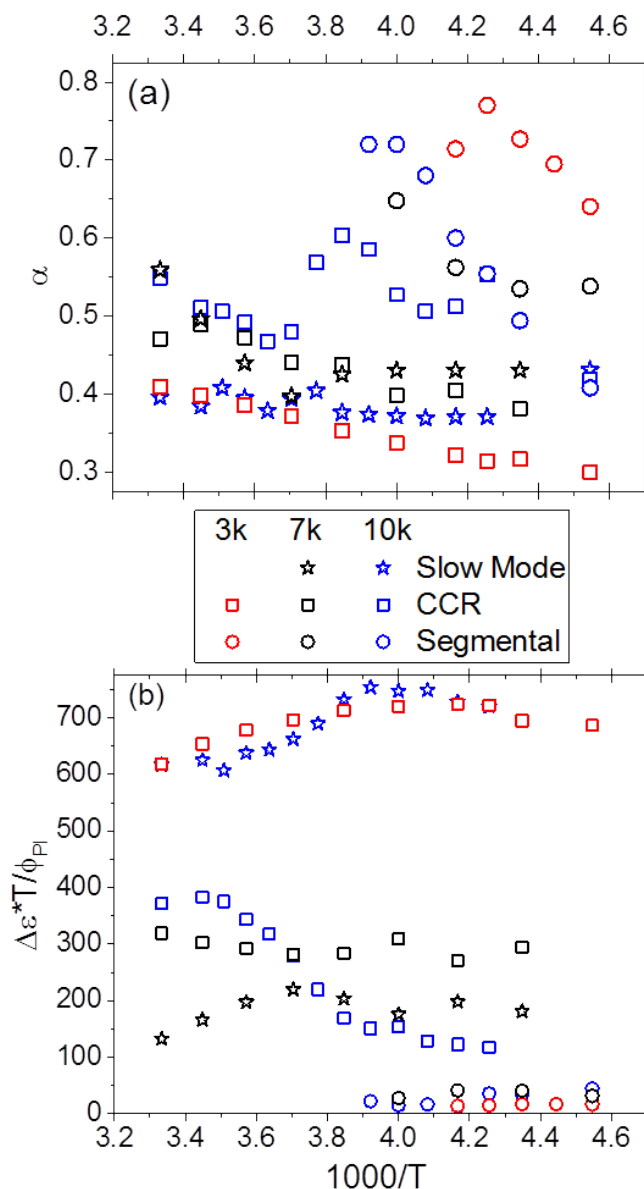


Figure 89: The temperature dependence of the shape parameter α (a), corresponding to symmetric broadening for the Cole-Cole fits to the segmental relaxation (circles), CCR (squares) and slow relaxation (stars) for confined 3k (red), 7k (black) and 10k (blue) PI. The dielectric strength, $\Delta\epsilon$, normalized by temperature and volume fraction of PI (ϕ_{PI}) from Eqn. 99 for is also displayed (b).

A decrease in α indicates a symmetric broadening in the distribution of relaxation times. Therefore, with increasing molecular weight there is an increasingly broadened distribution of relaxation times for the chains or portions of chains contributing to this CCR process and a narrowing of relaxation time distribution of the CCR with decreasing temperature for all molecular weights.

A careful analysis of the dielectric relaxation strengths, $\Delta\epsilon$, for each relaxation fit by Eqn. 99 below reveals unique and unexpected effects of confinement on the dynamics of the chain. The $\Delta\epsilon$ values for all processes are normalized by temperature and PI volume fraction (ϕ_{PI}) as estimated using a 7% porosity of the silica pores (see Fig. 88b). The dielectric relaxation strength of the chain relaxation is given by

$$\Delta\epsilon = \frac{4\pi N_a \mu^2 \phi_{PI}}{3k_B T M} F\langle R^2 \rangle \quad 99$$

where n is the average number density of dipoles, μ is the dipole moment, ϕ_{PI} is the volume fraction of dipoles contributing to the relaxation, $\langle R^2 \rangle$ is the chain dipole end-to-end distance, M is molecular weight, k_B is the Boltzmann constant, and T is absolute temperature. This normalization by ϕ_{PI} and temperature reveals segmental relaxation $\Delta\epsilon$ values for the confined polymers that are equal to those observed in the bulk for all molecular weights (see Fig. 90 for bulk $\Delta\epsilon$). Similar segmental relaxation strength, $\Delta\epsilon$, in bulk and normalized segmental relaxation under confinement corresponds to a constant average number density (n) of PI segments in each measurement.

The fact that these normalized $\Delta\epsilon$ values under confinement are comparable to the bulk systems suggests that the average number density of PI segments measured are similar under confinement as they are in bulk, and also indicates the pores are completely filled with PI. The normalized $\Delta\epsilon$ for the CCR is observed to be inversely proportional to molecular weight at low temperatures. For confined 7k and 3k PI, these values are relatively temperature independent, as are the strengths of the chain relaxations for all systems in bulk as shown in Figures 89 and 90.

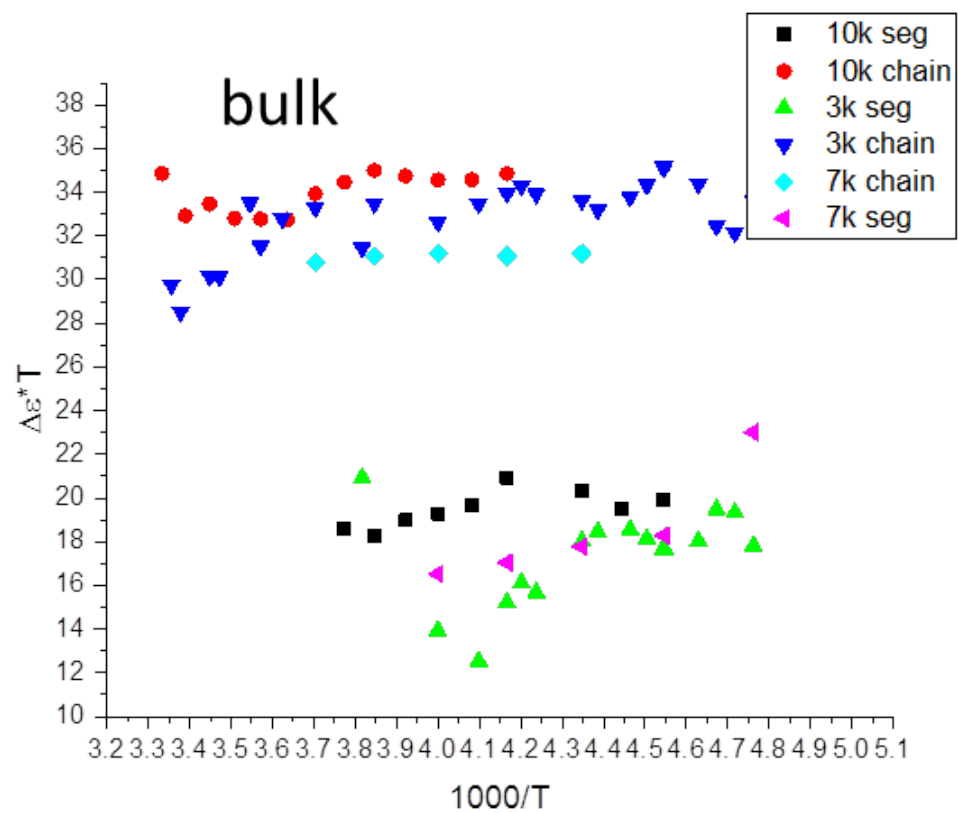


Figure 90: Temperature dependence of normalized dielectric strengths of PI in bulk.

On the other hand, for the 10k PI in pores, the $\Delta\epsilon$ decreases with decreasing temperature. This temperature dependence of the normalized 10k PI $\Delta\epsilon_{CCR}$ suggests that the end-to-end distance of the 10k PI is decreasing with decreasing temperature. This is further explained through analysis of the 10k PI slow chain mode.

The normalized $\Delta\epsilon$ of the slow chain mode (not obvious for the confined 3k PI) for the confined 10k PI is 2-4 times higher than that measured for the 7k PI. This increase suggests an increase in the average end-to-end distance of the 10k PI chain under nanoscale confinement compared the 7k causing the chain to take on more non-ideal conformations within the pores. This non-ideal conformation under confinement presumably results in a portion of the dipole moments in the chain to oriented by the spatial confinement leading to this slow relaxation for the 7k and 10k PI. The spectral shape of this slow relaxation is slightly broadened for the 10k PI compared to the 7k, and both shapes are temperature independent. The *total* normalized dielectric strength (summation of $\Delta\epsilon$ for the CCR and slow relaxation for the 7k and 10k, and $\Delta\epsilon_{CCR}$ only for 3k) for the confined 7k and 3k PI is determined to be roughly one order of magnitude higher compared to the strength of the chain relaxation of all systems in the bulk (data not shown). This suggests that the sum of these two processes in the 7k encompasses the same relative number of chain segments contributing to the end-to-end dipoles measured as for the 3k under confinement. However, for the 10k, in addition to the changes in the temperature dependence of the $\Delta\epsilon$, the *total* normalized dielectric strength of the CCR and slow relaxations together is roughly twice that compared to the 3k and 7k PI. We suggest that this also reflects an increase in the change of R_g relative to M when the molecular weight is increased to 10k. This is supported by evidence from simulations that during polymer translocation through a nanopore, if the size of the chain is large compared to the pore size, the polymer maintains an extended conformation during translocation, while smaller chains are able to reform their bulk-like coil once inside the pore and maintain this coiled

conformation until it escapes[383]. Overall, these changes in the PI dielectric relaxations within 6.5nm pores show that as the confinement becomes more extreme the dynamics of the polymer chain are significantly altered compared to previously reported systems that are confined at length-scales much larger than the polymer chain itself.

The average relaxation rates for the processes fit by Eqn. 97 are displayed against inverse temperature in Figure 91. The segmental relaxation in the confined systems has a weaker temperature dependence compared to bulk. This suggests a decrease in the relaxation time associated with the structural relaxation (*i.e.* a decrease in the dynamic glass transition temperature, T_g). This is consistent with changes in T_g for confined low molecular weight glass formers[372, 375]. The rates for the segmental motions decrease with increasing molecular weight in both the bulk and under confinement. This increase in segmental relaxation times with molecular weight is consistent with the increase in T_g with molecular weight for unentangled systems as extensively discussed in the literature[46].

The mean chain relaxation rates for the bulk polymers slow down with increasing molecular weight in accordance with the predictions of the Rouse model for nonentangled chains[9]. The average CCR rates for confined 3k PI in nanopores are very similar, but slightly slower compared to that observed in the bulk. As discussed before, this relaxation is significantly broadened under confinement. This relaxation rate also decreases faster with decreasing temperature compared to the bulk and has a slightly more Arrhenius-like temperature dependence. This dependence is typically discussed in terms of lower fragility. However, the global fluctuations, such as the dynamics of the polymer chain, govern the rubbery plateau and viscoelastic flow. Therefore, this more Arrhenius-like temperature dependence can be considered in terms of less cooperativity of intra- and inter-chain motions allowing for increased viscoelastic flow of the 3k polymer under confinement and is likely due to interactions with chains near the interface.

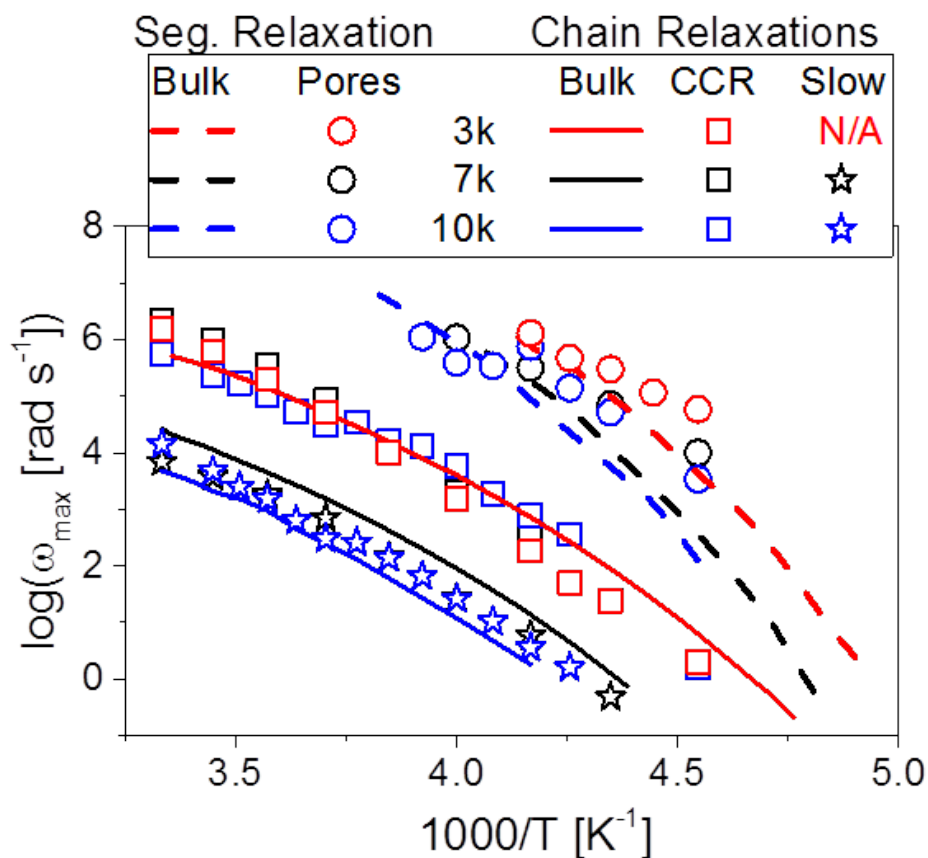


Figure 91: The relaxation rates from all fits to dielectric spectra using Eq. 97 for the 3k (red), 7k (black) and 10k (blue) PI systems versus inverse temperature. Lines represent bulk relaxations of the polymer segments (dashed) and chains (solid). Symbols represent the segmental relaxation (circles), CCR (squares) and slow relaxation (stars).

This is consistent with two recent findings in the literature: 1] The diffusivity of confined polymers increases due to a decrease in the possible pathways (*i.e.* increased tortuosity) of dynamical motion of polymer chains[384]; and 2] a lowered chain density under confinement due to interfacial adsorption[354]. Therefore, we speculate that there is higher free volume per chain and increased diffusivity of all of the PI M_w within nanopores. Furthermore, the similarity in the time-scales associated with the 3k chain in bulk and within pores suggests that the effects of surface interactions on dynamics is more influential than the geometric confinement itself at this degree of confinement. Here, we acknowledge recent reports of polymer films and polymers confined within hard cylinders and in polymer thin films that show that equilibrium chain conformations are reached after very long annealing times[343, 344, 385, 386]. The dynamics described in these reports suggest that these equilibrium states after long times are not governed by changes in the timescales relating to the dynamic glass transition but are more closely related to timescales associated with adsorption and desorption which are much slower than viscoelastic flow[341, 344]. As significantly long times were reported for these equilibrium effects to take place (from a week and up to one month), this was beyond the primary goal of the present study. Additionally, by maintaining a constant pore size, we are assuming the surface area of the polymers in contact with the pore surface is held constant, while varying the molecular weight changes the relative number of segments contributing to the end-to-end chain relaxation causing the bimodal distribution of the chain relaxation into the CCR and slow relaxation in the 7k and 10k PI under confinement. However, we conjecture that, if given ample time, the structural/segmental PI relaxation rates may approach that of the bulk, but the chain relaxations will still be altered by the geometric confinement. We will now explore this point further by discussing the relaxation rates of the more confined, higher molecular weight PI.

The slowest relaxation observed for both 10k and 7k PI under confinement, but not in the 3k PI, becomes more apparent as a low frequency shoulder to the

primary CCR relaxation with increasing molecular weight. The average rates of the slow relaxation for the 7k PI are decreased compared to the normal mode of the bulk 7k PI. Slowed Rouse chain dynamics of confined polymers compared to bulk have been previously described through dynamical ^1H NMR and neutron scattering studies for pore sizes much greater than the dimensions of the chain[362, 387, 388]. At timescales similar to that of the 7k PI slow relaxation, the slow relaxation of the 10k PI is observed. However, this relaxation is actually faster than its corresponding 10k chain relaxation in the bulk. The relative rates of the bulk chain relaxation divided by the slowest chain relaxation rates of all of our polymers in the pores is displayed in Figure 92.

Here, we assume that the timescales of the 3k PI CCR are the slowest observed for this system. This ratio decreases with decreasing temperature for the 10k PI, but increases slightly for the 3k and 7k PI. For nanoconfined amino terminated and native PPG in native silica and silanized silica pores, respectively, this ratio is also observed to decrease with increasing confinement[354]. As such, we use a length-scale ratio of the pore diameter to the radius of gyration (D/R_g) of the bulk polymer to describe the degree of confinement.

The R_g for our PI polymers was estimated from the hydrodynamic radius of PI in dioxane[389]. For the 3k, 7k, and 10k PI systems, the respective D/R_g ratios are found to be 3.4, 2.3 and 1.9, respectively. For systems with large D/R_g (> 2.5) the resulting chain dynamics have been reported to have similar relaxation timescales as observed in bulk[357]. As D/R_g decreases, the degree of confinement increases; thus, our results reveal that the timescales associated with the polymer chain dynamics increase faster with temperature compared to the chain relaxation in bulk. We observe that at $D/R_g \sim 2$, the average slow chain relaxation rates become faster than that of the bulk. This was observed, but not highlighted or discussed in the recent report of PPG under confinement, and we compare these data in Figure 92[354].

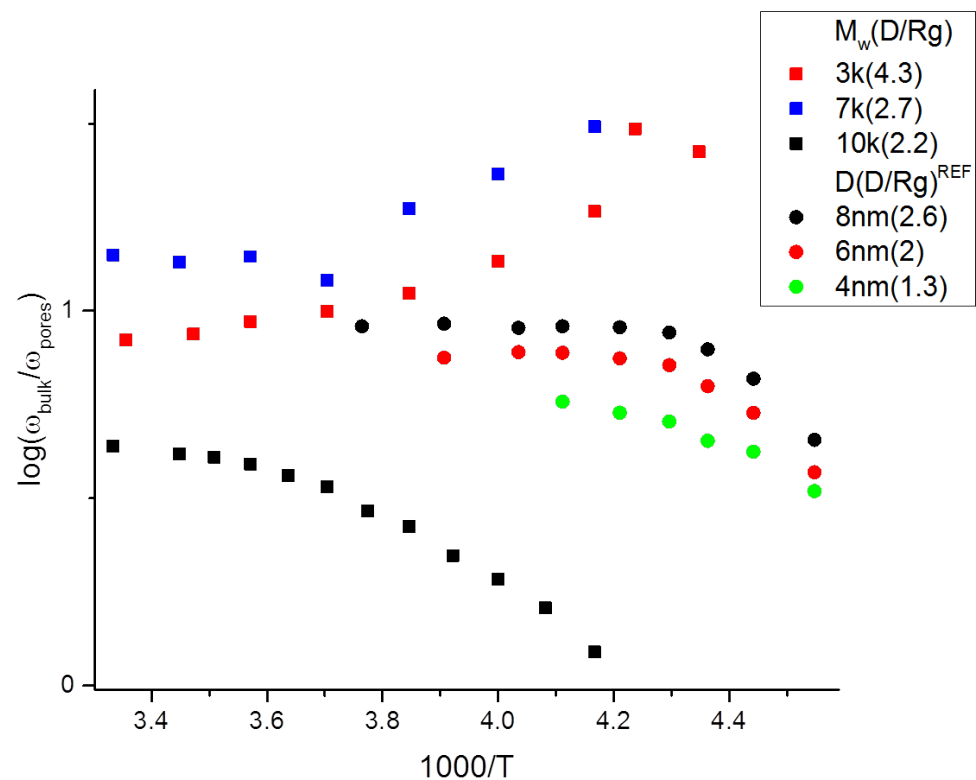


Figure 92: The temperature dependence of the ratio between the bulk chain relaxation rate and the slowest relaxation rate observed for each polymer confined within 6.5 nm silica nanopores and compared to reported literature data on confined PPG[354].

The main result of the current article is that at extreme confinement length-scales, the relative rates of the chain dynamics under confinement begin to increase faster with temperature compared to bulk. Thus, we suggest that below $D/R_g \sim 2$ the degree of geometric confinement becomes an influential factor in the conformation of the polymer chains apart from just effects of interfacial interactions on segmental motion.

Conclusions

We have presented results from dielectric studies of low molecular weight poly (*cis*-1,4-isoprene) (PI) in bulk compared to identical systems in unidirectional silica nanopores with average diameter of 6.5nm. The average size of the polymer chains as reflected by the radius of gyration (R_g) at these length-scales become comparable to that of the confining pore diameter. The only changes in the segmental dynamics observed under confinement are the temperature dependence corresponding to the speeding up of the dynamic glass transition. However, a slow dielectric relaxation is observed with increasing molecular weight, while a primary chain relaxation occurs for all polymers at timescales similar to that of the normal mode in bulk 3k PI. The relative rates of the slow relaxation compared to bulk in the 7k and 10k PI under confinement are observed to change significantly. Additionally, the dielectric relaxation strengths of the less confined 3k and 7k PI are comparable in contrast to that of the confined 10k PI. Furthermore, there is a decrease in dielectric relaxation strength with decreasing temperature for the 10k PI under confinement that we attribute to an increase in non-ideal chain conformations. Our primary observation is that a length-scale ratio of the pore diameter to the radius of gyration (D/R_g) at and below ~ 2 corresponds to a dramatic change in polymer dynamics due to extreme confinement of the polymer chains forced to orient in non-ideal conformations. We propose that the geometric confinement of polymer chains at this length-scale ultimately becomes more influential on the chain dynamics compared to interfacial adsorption effects.

Chapter 8: Polymerized Ionic Liquids in Silica Nanopores with Native and Modified Surfaces

A version of this chapter was originally published by Thomas Kinsey, Kaitlin Glynn, Tyler Cosby, Ciprian Iacob, and Joshua Sangoro in ACS Applied Materials and Interfaces. Permission to reproduce the paper below was given by copyright 2020 American Chemical Society. The publication did not include the discussions included here for the materials confined in silica nanopores with modified surface chemistries.

Kinsey, T., et al., *Ion Dynamics of Monomeric Ionic Liquids Polymerized In Situ within Silica Nanopores*. ACS Applied Materials & Interfaces, 2020. **12**(39): p. 44325-44334.[390]

Etching of the silica nanopores were performed by TK with instruction/guidance from TC and CI. Pore filling and polymerizations were performed by TK and KG. Surface modifications were performed by Zac Word (data not included in publication but are included in this chapter). All BDS and Raman measurements were performed by TK. The data was analyzed by TK with help from TC. Manuscript was written primarily by TK with edits, comments and suggestions from KG, TC, CI and JS. JS provided funding for this project. The final three paragraphs of the Results and Discussion covers dielectric studies of a the 1-ethyl-3-vinyl NTf₂ ionic liquid monomer polymerized in pores with various surface modifications. These studies are conditionally conclusive based on the amount of monomer that was converted to polymer following polymerization in the pores. These data were not able to be collected due to COVID-19 shutdowns in 2020.

Abstract

Polymerized ionic liquids are a promising class of versatile solid-state electrolytes for applications ranging from electrochemical energy storage to

flexible smart materials that remain limited by their relatively low ionic conductivities compared to conventional electrolytes. Here, we show that the *in-situ* polymerization of the vinyl cationic monomer, 1-ethyl-3-vinylimidazolium with the bis(trifluoromethanesulfonyl)imide counter anion, under nanoconfinement within 7.5 ($\pm$ 1.0) nm diameter nanopores results in a nearly 1000-fold enhancement in the ionic conductivity compared to the material polymerized in bulk. Using insights from broadband dielectric and Raman spectroscopic techniques, we attribute these results to the role of confinement on molecular conformations, ion coordination and subsequently, the ionic conductivity in the polymerized ionic liquid. These results expand the understanding of the dynamics of nanoconfined molecules and show that *in-situ* polymerization under nanoscale geometric confinement is a promising path towards enhancing ion conductivity in polymer electrolytes.

Introduction

By combining the robust mechanical properties of polymers with the ion conduction capabilities and electrochemical stability of room temperature ionic liquids (ILs), polymerized ionic liquids (polyILs) have emerged as a promising class of highly tunable materials for a wide range of applications including battery technologies, fuel cell membranes, CO₂ capture, biomolecule detection, nano-actuators, and stimuli responsive materials[391-394]. The fast ion diffusion compared to the timescale of the structural dynamics of the polymer segments is the main distinguishing characteristic of these materials compared to typical solid polymer electrolyte systems[395]. However, the effective immobilization of one of the ions onto the polymer backbone following polymerization drastically reduces the overall ionic conductivity compared to the un-polymerized ILs. Other changes in physicochemical properties that result from polymerization include a decrease in molecular degrees of freedom and increased viscosity, both of which affect ion mobilities[396, 397]. There have been several attempts to increase ionic

conductivity in ILs through various chemical and physical methods, one of which is the use of physical confinement at nanometer length-scales[398-401]. However, the effects of physical confinement at the molecular level on the properties of polyILs and the question whether it is possible to achieve high ionic conductivity through geometric nanoscale confinement remain unexplored.

Geometric confinement at the molecular level is known to result in significant changes in the physical properties of various glass forming systems by altering the length-scales of cooperative dynamics and/or increasing the role of substrate interactions[220, 354, 402-404]. Additionally, the behavior of ions in nanopores is of great importance for engineering nanofluidic and biosensing devices, and the mechanism of ion transport through nanochannels is of much interest for biomimetic technology such as cellular transistors and selective filtration[405-409]. For pure ILs under nanoconfinement, reports have identified that both influences from the length-scale of the confinement and from the electrostatic surface interactions of the ions with the substrate can either facilitate or hinder ion transport[410-413]. Experimental and simulation studies of ILs have suggested that there is an increase in the coordination between the anion and cation near the substrate which can result in slowed ion diffusion compared to bulk[399, 414]. Furthermore, ordered solvation layers of up to several ion pairs, which also correspond to a reduction in ion mobility, have been shown to occur under confinement and near the substrate interface due to these electrostatic surface interactions of the ILs and the substrate[415-418]. On the other hand, faster dynamics in nanoporous media have also been observed as the confinement length-scale increases and the strength of interactions with the substrate decreases[353, 358]. These faster dynamics with increasing confinement have been utilized to help design synthetic biomimetic ion-channels and polymer based nanofluidic diodes[407, 419, 420]. Finally, the conformational equilibrium structures of the IL moieties have been observed to change under confinement which may also alter dynamics[421, 422]. Therefore, nanoscale

confinement seems to be a promising approach to tune physicochemical properties of polyILs.

For non-charged polymers under nanoconfinement, several physical characteristics have also been observed to change compared to bulk including the dynamic glass transition temperature (T_g), self-diffusivity, dielectric relaxation strength, conformational entropy, and molecular packing density[151, 221, 343, 354, 384, 385]. Similarly, these structural and dynamical effects that are observed under nanoconfinement have also been observed in pressure-dependent studies of non-charged polymer systems[47, 403, 423-426]. Additionally, *in-situ* free radical polymerization within anodized aluminum oxide (AAO) nanopores have resulted in an increase in reaction kinetics with the resulting polymers exhibiting a narrower molecular weight distribution compared to those prepared under similar reaction conditions in bulk[351, 427]. For bulk polyILs, experimental and computational studies have shown that when the ion conduction is dominated by hopping of ions along the polymer backbone corresponding to faster dynamics compared to hopping from chain to chain in an entangled system[426, 428, 429]. Thus, if nanoscale confinement can lead to favorable alignment of chains as seen in non-charged polymers, then higher ionic conductivity may result in polyILs. However, very few studies have examined the effects of surface interactions and confinement on the properties of polyILs[351, 428, 430].

To unravel the interplay between confinement on the molecular conformations and ionic dynamics of nanoconfined polyILs, the well-studied monomeric vinyl IL, 1-ethyl-3-vinylimidazolium [1E3VIm] with the bis(trifluoromethanesulfonyl)imide [NTf₂] counter anion, was filled into unidirectional nanoporous silica membranes with mean pore diameter of 7.5 nm, and subsequently polymerized *in situ* by free radical polymerization. Broadband dielectric spectroscopy (BDS) and Raman spectroscopy were employed to study the changes in the dynamics and ion conformations and coordination that result from both the nanoconfinement and polymerization. The ionic conductivity of the

confined polyIL was observed to increase by a factor of ~ 1000 compared the bulk equivalent. We attribute the enhancement in charge transport of the confined polyIL to changes in the equilibrium ratio of the NTf₂ *cis* and *trans* conformational isomers and decreased coordination between cations and anions. We demonstrate that these changes arise from (i) screened electrostatic interactions of the substrate with the free anions, (ii) lower packing density of the polyIL within the pores, and (iii) implicit unidirectional alignment of polymer chains within the nanopores that result in increased mobility of the NTf₂ anion.

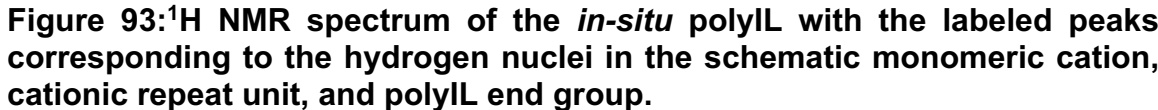
Materials and Methods

The unidirectional, 50 μ m-thick nanoporous silica membranes with an average diameter of 7.5 (± 1.0) nm and $\sim 7\%$ porosity were prepared by an electrochemical etching of p -, highly-doped silicon wafers in an electrolyte of 1:1 volume ratio of hydrofluoric acid:ethanol as previously described[348]·[358]. Hydrofluoric acid (HF) is corrosive and extremely toxic. Therefore, proper personal protective equipment should be worn, safety protocols followed, and training completed before and while handling HF. Anodization and electropolishing steps were performed using 140 mA at 35V for 40min and 5A at 15V three times for 30s each, respectively. Subsequent oxidation of the nanoporous silicon wafers was performed at 700°C for 3h, then 880°C for 6h. 1E3VIm NTF₂ at 98% purity was purchased from Iolitec and dried at 125°C and 10⁻³ mbar for 24h before use.

The free radical thermoinitiator, azobisisobutyronitrile (AIBN), was purchased from Fisher and recrystallized from methanol. The AIBN was mixed with the IL at 1.3 wt% AIBN for 24h at room temperature, then oxygen was removed by bubbling the solution with dry N₂ for 40min. The IL, with or without AIBN, was filled into the nanoporous silica by coating each side of the membrane with the liquid then placing it in an ultra-high vacuum chamber and holding it at $<10^{-8}$ mbar at room temperature for 48h. The sample was then removed from the vacuum oven and any excess liquid from the surface was carefully removed by wiping with

Kimwipes then subsequently sheared multiple times between two clean glass slides until no detectable residual IL was transferred from the membrane surfaces to the slide. Free radical polymerization in nanopores was performed in triplicate by placing the cleaned IL-filled membrane into a Linkam THMS600 Temperature Stage which was then purged for 30 min with dry N₂ before heating the material to 85°C and holding for 24h at the same temperature. The pure polyIL in bulk was polymerized during Raman spectroscopy with the same conditions as the *in-situ* polyIL: solvent free with 1.3mol% AIBN at 85°C in the Linkam stage. This bulk polymerization was performed in triplicate and the conversion curve for each experiment was reproducible within $\pm 1\%$. The resulting confined polymers' M_n were determined to be ~ 3 kg/mol by crushing the membranes that contained and extracting the material with d₆-DMSO and analyzed with end group analysis using ¹H NMR spectroscopy (see Fig. 93). The bulk polyIL was determined to have M_n = 5.2 kg/mol. As described in the Results and Discussion, the maximum conversion of monomeric 1E3VIm monomer to polymer was $\sim 75\%$ within the pores. Therefore, a bulk blend was prepared for measurement comparisons by preparing a mixture with 25 mol% monomeric 1E3VIm NTf₂ with a 3.2 kg/mol poly1E3VIm NTF₂ in tetrahydrofuran at room temperature and stirring for 12h. The mixture was subsequently dried under vacuum at 85°C for 48h to remove the solvent.

Raman spectroscopy measurements were performed with a Horiba LabRAM HR Evolution Raman microscope fitted with a liquid nitrogen cooled charge coupled detector and a 648nm excitation laser, 1800 gratings/mm over five 2s accumulations. A 100x objective was used for all measurements except when using the N₂ purged temperature stage for temperature dependent measurements of solvent free, bulk polymerization of 1E3VIm NTf₂ and subsequent temperature dependent measurements. In this case, a long working distance (LWD) 20x objective was used



. The measurement of the solvent free, bulk polymerization was prepared by placing the 1.3 wt% AIBN/IL mixture between two glass cover slips with 0.3 mm thick Teflon spacers to maintain sample thickness and purging the temperature stage for 10min with dry N₂.

The temperature was raised quickly to 85°C following the N₂ purge to initiate free radical polymerization and held at 85°C to ensure the resulting polyIL was above its T_g throughout the reaction during bulk polymerization measurements^[391]. Temperature dependent measurements were made only after the C=C stretching mode of the vinyl monomer at 1660 cm⁻¹ had disappeared for 30 min indicating no further detectable conversion of the C=C bond into the polymer backbone was occurring^[431, 432]. All Raman spectra were normalized by the intensity of the S-N-S bending mode of the NTf₂ anion, I₇₄₀, to control for changes in the density of the material during the reaction^[433, 434].

Dielectric experiments were performed using a Novocontrol High Resolution Alpha Dielectric Analyzer with an applied ac voltage of 0.1V over the frequency range (10⁻¹-10⁷ Hz). Temperature was controlled with Quatro cryostat system (180 K-400 K with a stability of ± 0.1 K). The bulk materials were sandwiched directly between two 10 mm diameter brass electrodes held at a constant thickness using two 200µm diameter glass rods. Nanopore samples were placed between two 6mm diameter, 0.75µm thick aluminum foil disks to ensure sufficient electrode contact with the silica membrane then paced between two 6 mm brass electrodes.

Results and Discussion

Prior to investigating the properties of the nanoconfined polyIL, it is critical to have a measure of the degree of polymerization, fraction of unreacted monomer, and extent of nanopore-filling in the native pores (surface modified pores will be discussed later). These factors are readily probed by confocal Raman spectroscopy and complementary ¹H NMR measurements. First, the progression

of free radical polymerization in bulk and nanoconfined 1E3VIm NTf₂ is investigated. Prior to further analysis, all Raman spectra were baseline corrected and normalized by the integrated intensity of the S-N-S bending mode of the NTf₂ anion, I_{740} , to account for changes in the density of the material during polymerization[433, 434]. The C=C stretching mode of the vinyl group on the cation shows up as a band at 1660 cm⁻¹ in the Raman spectrum[431, 432]. As shown in Figure 94 of the full Raman spectrum (200 – 2000 cm⁻¹), this peak reduces in intensity following polymerization due to reaction of the vinyl bond into the polyIL backbone. An *in situ* measurement during bulk polymerization was also performed (see Fig. 95a) to calculate the percent conversion of the monomeric cations into polymeric repeat units within the chain backbone over time (*i.e.* polymer fraction = $[I_{t=0} - I_t] / I_{t=0}$, where I_t is the integrated intensity of the normalized 1660 cm⁻¹ peak at initial time, $t=0$, and as time progressed during polymerization). These polymer fraction data are displayed as a conversion curve in the inset of Figure 95a and reveal a final monomer percent conversion in bulk of ~95%. The resulting polymer was measured by ¹H NMR to determine the number average molecular weight of $M_n = 5.2$ kg/mol.

Using the data in the inset of Figure 95a as a calibration basis for polymer fraction, the percent conversion of monomeric cations into polymer repeat units under nanoconfinement was determined to be 72 (4) % over three separate experiments (see Fig. 95b). The data of a Z-mapping spectrum using confocal Raman microscopy of the polymerized 1E3VIm NTf₂ in the nanopores, with an accuracy of ±50 nm, is displayed in Figure 95d. The depth profile of the normalized I_{1660} in Figures 95c and 95d reveals that the resulting polymer and unreacted monomer are uniformly filled through the pores after polymerization. Assuming no termination by combination, the M_n of resulting polymer was estimated to be ~3 kg/mol by ¹H NMR from the data in Figure 93.

For comparison, a bulk blend of a $M_n = 3.2$ kg/mol polyIL was prepared with 75 mol% monomer as described in the Materials and Methods section.

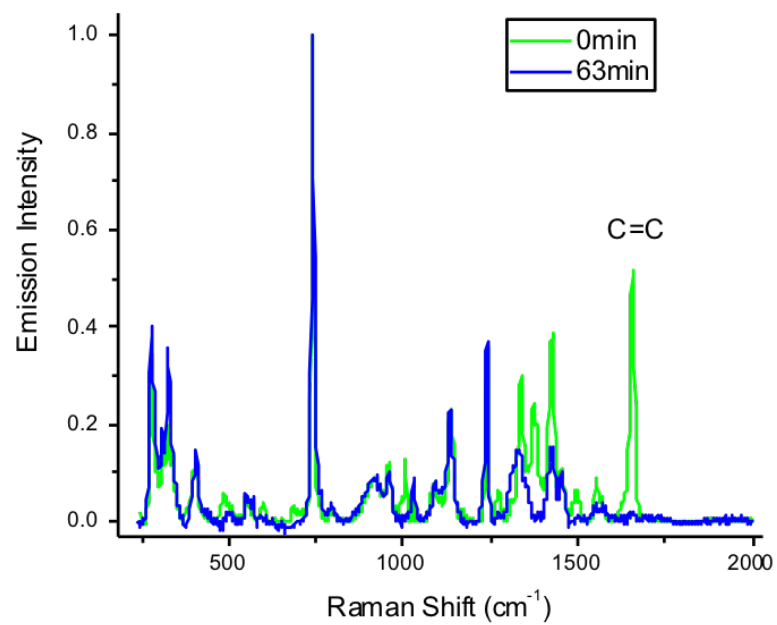


Figure 94: Raman spectrum of non-normalized data prior to and following bulk polymerization.

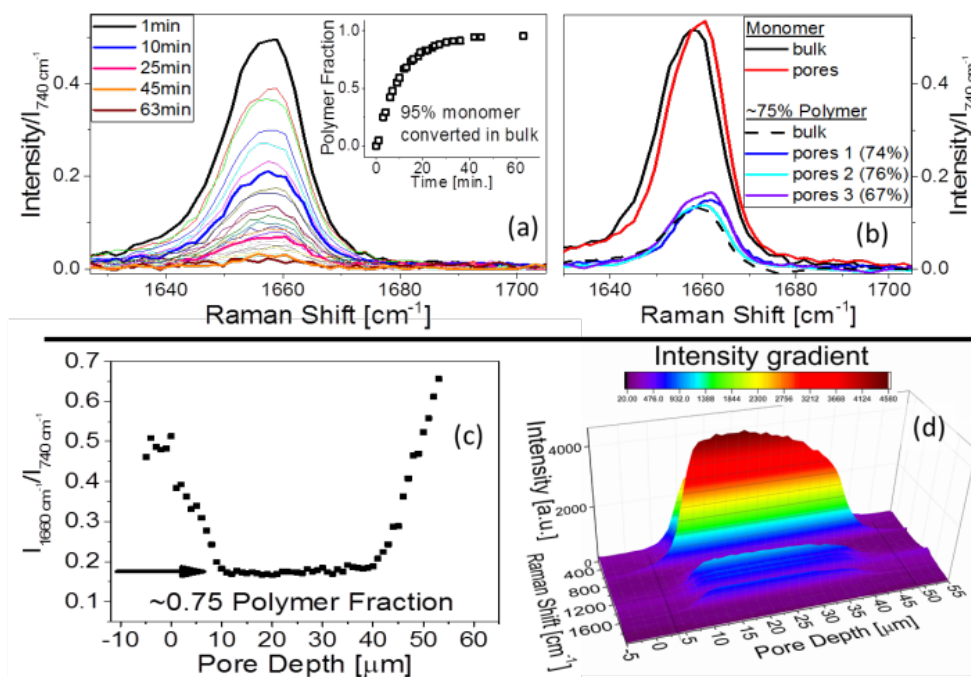


Figure 95: Normalized Raman spectra showing decreasing intensity of the of the 1660 cm^{-1} band over time during bulk polymerization (a), as well as before and after *in-situ* polymerization and bulk 75% polyIL/IL blend (b). The inset of (a) shows that the calculated polymer fraction during bulk polymerization over time with a final monomer conversion of 95%. Confocal Raman Z-mapping normalized by I_{740} after polymerization within pores (c) and non-normalized 3D data plot (d) reveals that the pores uniformly filled pores with IL and polyIL.

Figure 95b shows that the intensity of the 1660 cm^{-1} peak for the bulk 75% polymer/monomer blend is comparable to that of the confined polymer sample. The bulk mixture and neat polyIL will be henceforth referred to as the “75% polyIL/IL blend” and “bulk polyIL”, respectively, and the nanoconfined IL and polymerized samples will be termed the “1E3VIm NTf₂ in pores” and “*in-situ* polyIL”, respectively.

From the BDS experiments, the real part of the complex conductivity (σ') and imaginary part of electric modulus (M'') are plotted against frequency in Figure 96 for all samples except for the bulk 75% polyIL/IL blend. The dielectric spectra of bulk materials result in qualitatively similar data with a characteristic frequency-independent plateau corresponding to the DC ionic conductivity (σ_0). The polymer and monomer confined within the nanopores, however, do not display a characteristic plateau for σ_0 . The most probable reasons for this are a distribution in pore sizes and mobility deviations at such small length-scales that cause an increased distribution of polarization timescales[351, 353]. Therefore, the M'' peak frequency (ω_c) is taken to denote the characteristic rate of the onset of long-range ion hopping, and the value of σ' at ω_c is used to estimate σ_0 for all samples except the bulk monomeric IL. The $\sigma'(\omega_c)$ values are typically higher than σ_0 by a factor of about 2 (see Fig. 96b), but are often used when the distribution of ion hopping relaxations is not clearly represented by a single onset frequency.

Below 240K the monomer in bulk crystallizes and σ_0 drops considerably and the timescales of ω_c occur outside the accessible frequency range. Therefore, the actual σ' plateau value, σ_0 , is taken as the σ_0 for this sample. Crystallization does not occur for any of the other samples in bulk or in pores, and, therefore, the $\sigma'(\omega_c)$ values are used as an estimation of σ_0 for relative consistency. In Figure 97, M'' and normalized σ'/σ_0 data from 190K-230K are plotted together as master curves by normalizing the angular frequency by ω_c for the *in-situ* polyIL and 1E3VIm NTf₂ in native pores.

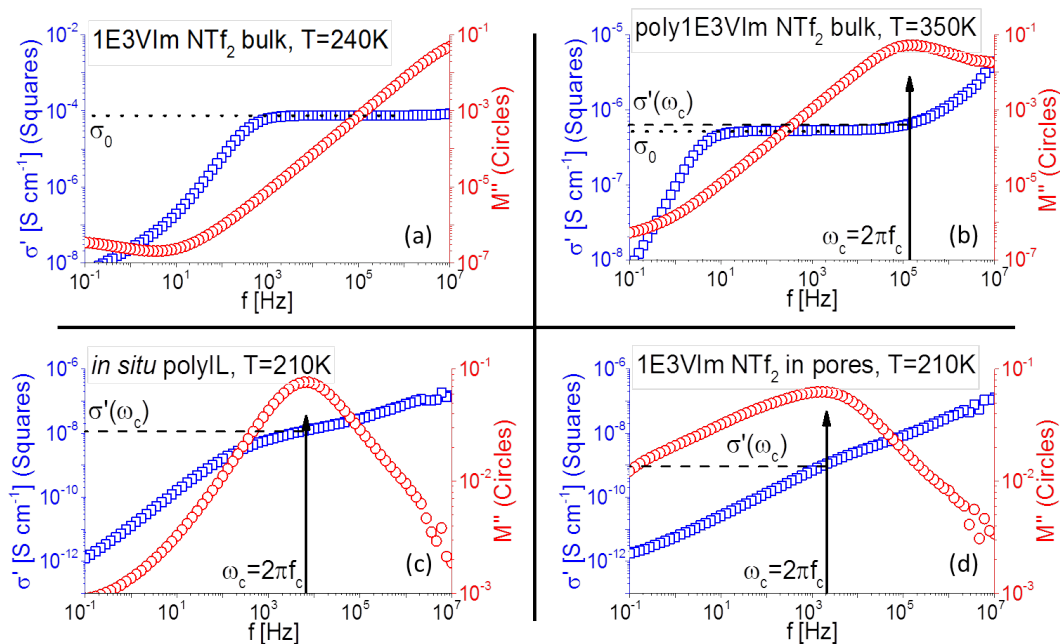


Figure 96: The frequency-dependent real part of the complex conductivity (σ' , left axis) and imaginary part of the electric modulus (M'' , right axis) versus frequency for bulk monomer at 240K (a), bulk polymer at 350K (b), *in-situ* polyIL at 210K (c) and 1E3VIm NTf₂ at 210K (d). The frequency of the peak maximum in M'' is indicated with vertical arrows at f_c . The horizontal dotted lines indicate the value of σ_0 for the bulk monomer and polymer samples. The dashed lines signify the σ' values at the frequency of the main M'' peak which corresponds to the onset of long-range ion hopping.

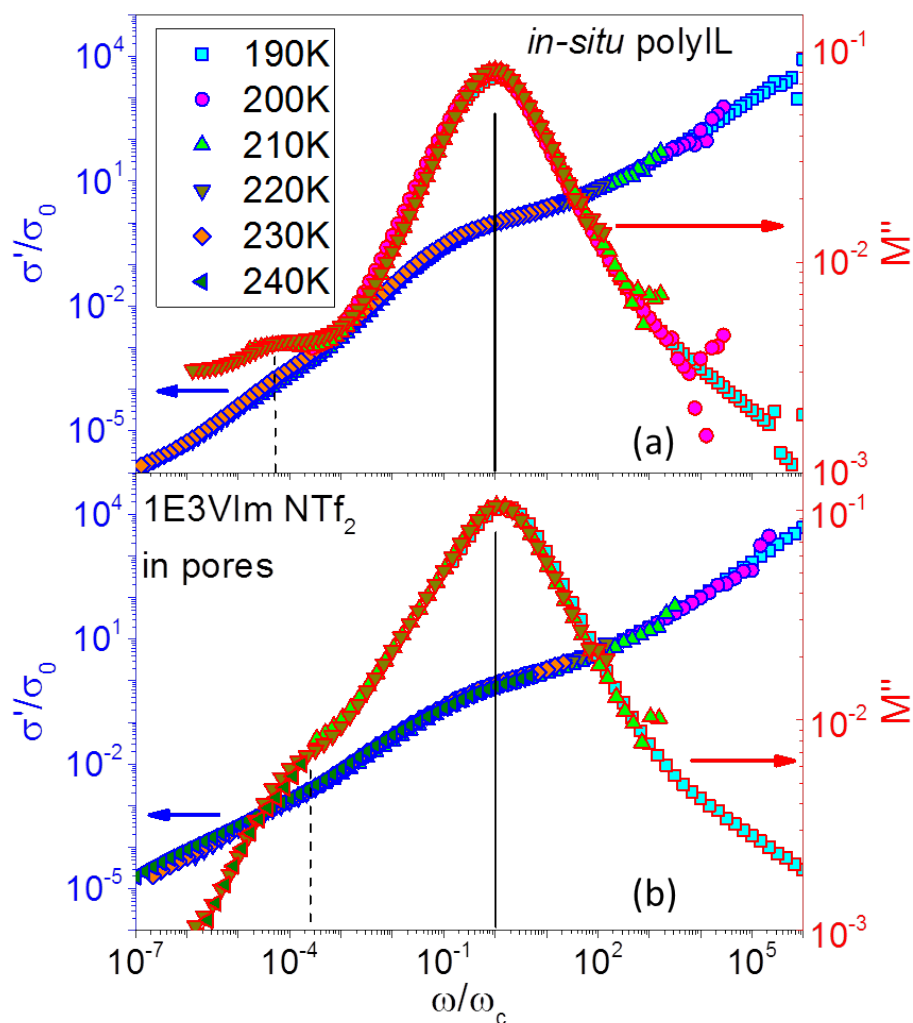


Figure 97: The master curves of the real part of the complex conductivity (σ') and the imaginary part of the electric modulus (M'') functions versus the radial frequency scaled by the characteristic ion transport rate (ω_c) for confined polymer (a) and monomer (b). The real part of conductivity (blue edged data) is normalized by the ionic conductivity, σ_0 (left axis). These master curves were prepared by normalizing the frequency dependent spectra at each temperature by ω_c . Vertical lines are added as guides to the eye, denoting the main peak at ω_c and the lower frequency peak of confined polymer and monomer ion dynamics, respectively.

This representation of M'' in Figure 97 shows that the breadth of the main peak is narrower for the *in situ* prepared polyIL compared to the 1E3VIm NTf₂ in the nanopores. This suggests a more homogeneous distribution of ion dynamics timescales for the *in-situ* polyIL samples. In the M'' master curves of Figure 97, another lower-frequency, higher-temperature peak is present with a weaker intensity than the $M''(\omega_c)$ relaxation for both the 1E3VIm NTf₂ in pores and *in-situ* polyIL. This relaxation is slightly perceptible as a low-frequency shoulder in the single temperature spectra of Figure 96d. This slower relaxation is ascribed to interfacial ion dynamics that are not observed in bulk, presumably arising from electrostatic interactions at the substrate interface[414].

The representative ionic conductivities are plotted versus inverse temperature for all materials in Figure 98, along with the σ' values associated with the lower frequency M'' peak for the samples confined within native silica pores which are labeled with “confined polymer” and “confined monomer”. The values for the *in-situ* polyIL and 1E3VIm NTf₂ in pores in Figure 98 are corrected for the 7% porosity of the silica membranes. As expected, the 75% polyIL/IL blend has a lower conductivity compared to the bulk IL with a similar Vogel-Fulcher-Tammann (VFT) temperature dependence, whereas the bulk polyIL displays an Arrhenius-like temperature dependence especially at low temperatures. This VFT-like temperature dependence suggests that at the 75% polyIL/IL blend concentration, the chain packing frustration in the pores may not be significant enough to have decoupled ionic conductivity from ion dynamics as observed in bulk [395, 397].

The linear relation in the log-log plot of σ_0 and ω_c (termed the Barton-Nakajima-Namikawa relation, BNN) holds for all samples as seen in Figure 99. The *in-situ* polyIL and 1E3VIm NTf₂ in pores are shown for all of the triplicate samples. The bulk polymer, bulk 75% polyIL/IL blend, and bulk-like conductivities for the monomer and polymerized samples in pores are shown as stars, crossed diamonds, and solid and open circles, respectively (with a solid line for a guide).

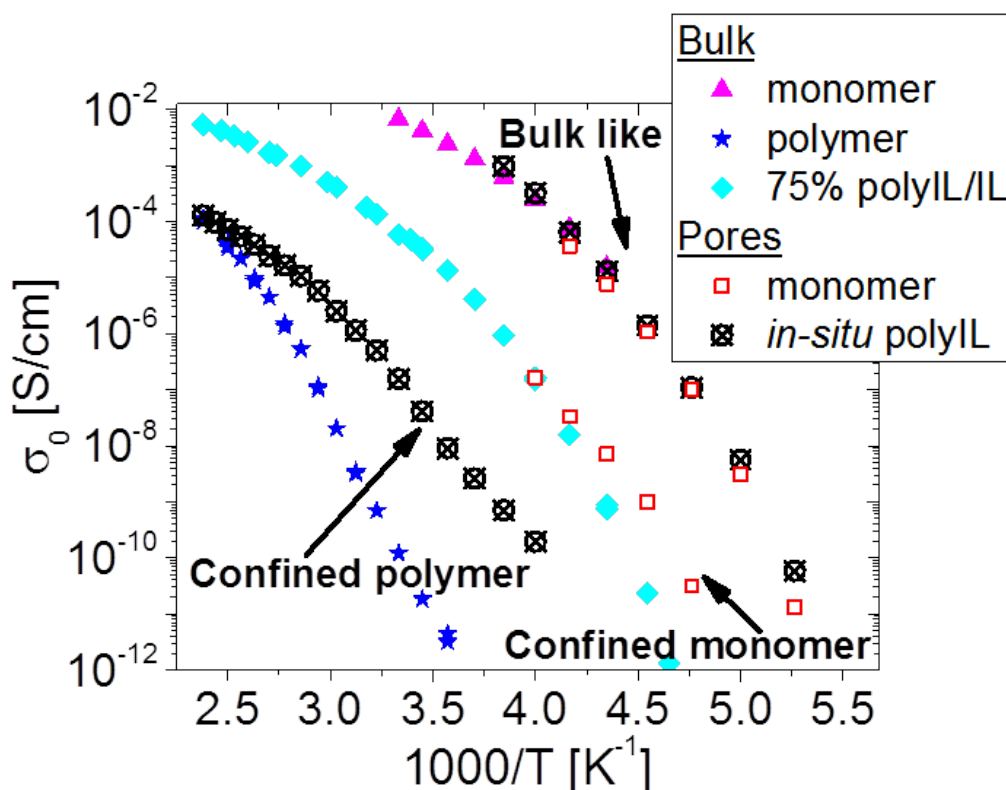


Figure 98: The dc ionic conductivity ($\sigma_0 \sim \sigma'(\omega_c)$) plotted against inverse temperature for all ILs and polyILs (see legend). For nanoconfined samples, the main $\sigma'(\omega_c)$ values are signified with the arrow denoting “bulk like” conductivities. The data labeled “confined polymer” and “confined monomer” are the σ' values that correspond to the lower-frequency, higher-temperature M'' peak shown in Fig. 97.

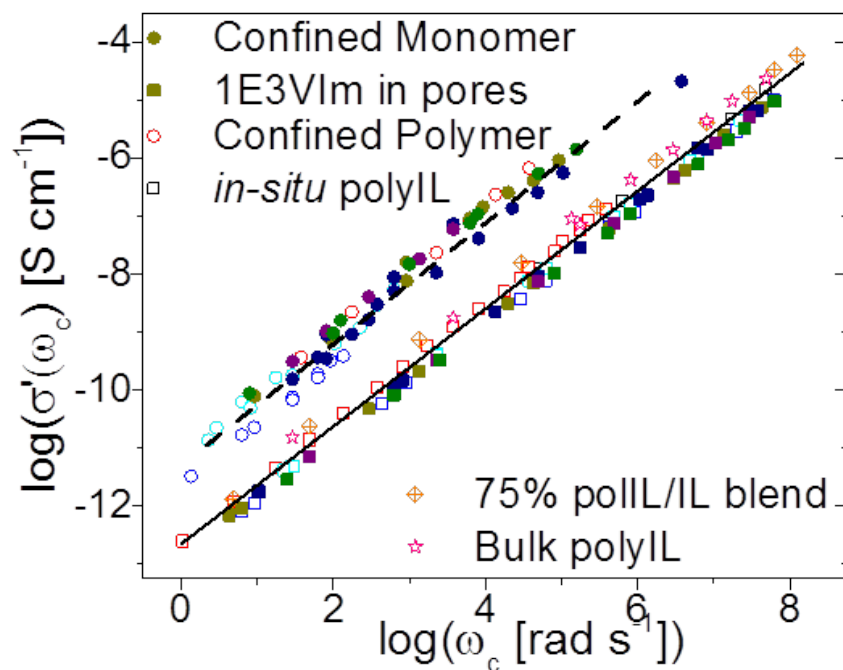


Figure 99: BNN plot for all triplicate samples in pores for the monomer and polymerized sample, and also for the polymer containing materials in bulk. The corresponding log conductivity vs 1000/T data are found in Fig. 98.

All of the data in Figure 99 fall on the same line and correlate with the BNN relation of the random barrier model of AC to DC ion conduction[435]. The “confined” monomer and polymer conductivities, as shown in Figure 99, are observed to have an increased value of conductivity for the corresponding ion hopping rate as observed in the closed and open circles (with a dashed line as a guide).

The ionic conductivity of the 1E3VIm NTf₂ in pores is similar to that in bulk and is consistent with past reports[351, 353, 358]. The “confined polymer” conductivity of the *in-situ* polyIL in Figure 98 is observed to be similar to the polyIL in bulk at high temperatures. However, since the “confined polymer” conductivity exhibits a decreased activation energy, the resulting ionic conductivity at room temperature is 3 decades greater than bulk polyIL. We attribute this result mainly to alignment of polymer chains through the pore allowing for single chain ion hopping mechanism which has been estimated by simulations to contribute to enhancement of ion transport compared to intra-chain hopping[436]. Through transport flux considerations, an equation for dc conductivity (σ_0) can be formulated as a linear combination of the products of mobility (μ), number density (n) and charge (q) of all the ions (i) in the system: $\sigma_0 = \sum_i \mu_i n_i q_i$. Following polymerization, it is reasonable to expect that the effective number density of charge carriers (n) would not differ by orders of magnitude. By assuming no effective change in the charge of each ion, the main contribution to increase the dc conductivity toward lower temperatures for the polyIL in the pores, therefore, must be the mobility of the ions (μ).

Additionally, the fact that there is an obvious bifurcation in the timescales of ion dynamics for the *in-situ* polyIL (bulk like and confined), which is not observed in the similar bulk material of the 75% polyIL/IL blend, strongly suggests heterogeneous dynamics of the polymerized 1E3VIm NTf₂ material within the silica pores. These heterogeneous dynamics will be explored further in the discussions on ion conformation and coordination below.

To investigate the roles of confinement and polymerization on the NTf₂ conformations and anion-cation coordination we will now return to the Raman data. The NTf₂ anion is known to take on both a *cis* and *trans* conformational isomers, which in the literature are called the C1 and C2 conformers, respectively, and are shown in the cartoon below Figure 100[421, 437-439]. In Figure 100a, the room temperature Raman peaks at 398 cm⁻¹ and 410cm⁻¹ that correspond to the C2 and C1 conformers, respectively, are displayed for all of the samples in this study. The relative integrated intensities of these peaks (*I*₃₉₈ and *I*₄₁₀) correspond to the conformational equilibrium concentrations of the NTf₂ *trans* and *cis* isomers[440]. The monomer samples, both in bulk and nanoconfinement, have a relatively decreased *I*₄₁₀ indicating that the monomer samples have a significantly decreased fraction of the C1 conformer, whereas the bulk polyIL and 75% polyIL/IL blend samples have an increased equilibrium concentration of this *cis* isomer. Interestingly, the *in-situ* polyIL is found to have a similarly low fraction of the C1 conformer as both of the monomer samples. In Figure 100c, the *cis* and *trans* isomer peaks at selected times measured during bulk polymerization at 85°C show that the relative amount of NTf₂ conformations shifts to a higher concentration of *cis* isomers as polymerization progresses. This shift occurs at ~10min following initiation and corresponds to a polymer fraction of about 0.7. Correspondingly, the 75% polyIL/IL blend at room temperature has a similar *I*₃₉₈ to *I*₄₁₀ ratio as the bulk polymerization at 85°C during Raman measurement at 10 min.

The increased equilibrium concentration of the C1 conformer in the bulk 75% polyIL/IL blend compared to an increased C2 conformer concentration for the *in-situ* polyIL is a direct result of confinement of the material within the pores, and will now be compared to experiments from the literature.

The equilibrium conformational changes of the NTf₂ anion are well documented in the literature for ILs and metal ion salts. Differences in equilibrium concentrations of the C1 and C2 conformer in NTf₂ containing ILs have been observed in crystalline domains and at higher pressures.

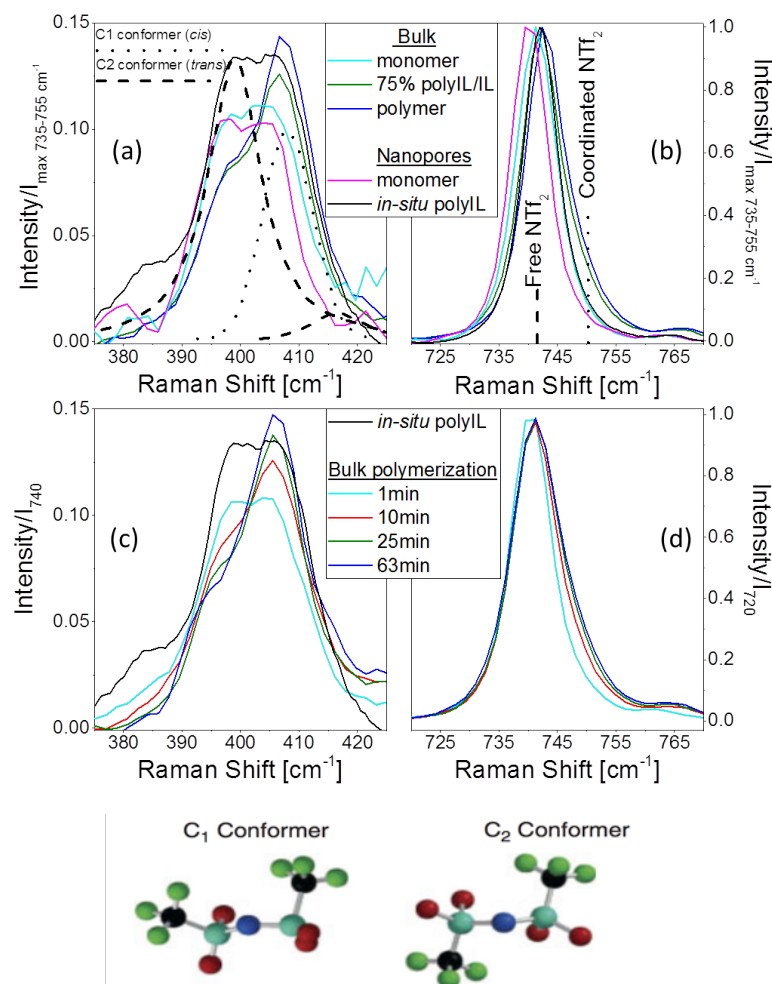


Figure 100: Raman spectra associated with the NTf₂ *cis* (dotted) and *trans* (dashed) conformations at 410 cm⁻¹ and 398 cm⁻¹, respectively, for bulk samples, monomer in pores and *in-situ* polyIL (a) and during bulk polymerization measurements (c). The S-N-S bending mode observed at ~740cm⁻¹ is displayed for all materials (b) and during bulk polymerization measurements (d). In (b) the dashed and dotted lines signify bands corresponding to free anions and more coordinated anions, respectively. All are normalized by peak intensity of the S-N-S bending mode at ~740cm⁻¹ to account for density variations among the samples. The cartoons below the plots show the two NTf₂ isomer conformations with the green, black, red, light blue and dark blue balls signifying hydrogen, carbon, oxygen, sulfur and nitrogen atoms, respectively.

On the other hand the C1 conformer has been calculated to have reduced conformational entropy and larger dipole moments[441, 442].

Additionally, it has been determined that packing density and conformation plays a crucial role in crystallization and glass formation of NTf₂ containing ILs^[423]. Therefore, these NTf₂ isomers can be used as a proxy for considering possible changes in the molecular density of the materials in this study. Furthermore, recent results of polymers confined to silica nanopores showed that for poly(propylene glycol), a density gradient of chain forms where lower densities occur at the center of the pore[354]. The same group also reported evidence of density fluctuations that determine the glassy dynamics of alcohols in nanopores from positron lifetime annihilation spectroscopy and BDS measurements[220]. Considering our results in combination with conformational and density changes reported in the literature, we conjecture that a higher NTf₂ equilibrium concentration of the C1 conformer in our materials can be qualitatively used as a proxy for determining which materials have a comparatively higher packing density. As such, the *in-situ* polyIL sample has a lower average packing density than the bulk samples that contain polyIL. This lower density within nanoconfinement then corresponds to relatively higher concentration of C2 conformers which also correspond to materials with the highest ionic conductivities (e.g. monomeric IL and nanoconfined materials).

Temperature dependent Raman spectroscopy for the bulk polyIL at selected wavenumbers is shown in the two panels of Figure 101. The right panel of Figure 101 shows the peaks discussed above for the *cis/trans* conformational isomers of the NTf₂ anion. The ratio of these two peaks are used to calculate the equilibrium conformational enthalpy change from *cis* to *trans* ($\Delta H_{\text{conf}} = 2.45$ kJ/mol) with increasing temperature as shown in the inset. This enthalpy changes is slightly decreased compared to the value for a similar monomeric ionic liquid in bulk from the literature (1-ethyl-3-methylimidazolium NTf₂, $\Delta H_{\text{conf}} = 3.5$ kJ/mol), and is likely due to the reduced degrees of freedom associated with the bulk polymeric system compared to the IL[440].

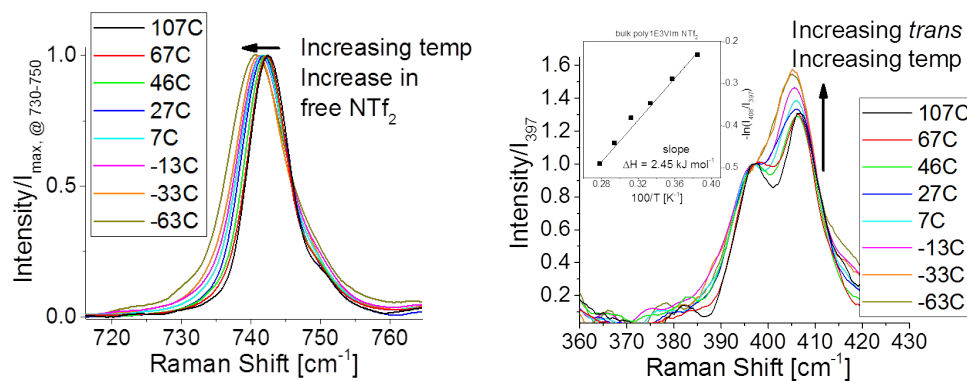


Figure 101: Temperature dependent Raman spectrum for the NTf_2 vibrational modes of the *cis-trans* isomers (right) and S-N-S bending mode (left). The inset of the right panel shows the data used to calculate the ΔH_{conf} of the bulk polyIL from the slope of the relative intensities of the two peaks.

Additionally, with increasing temperature the S-N-S bending mode of the anion in the left panel of Figure 101 shifts toward higher wavenumbers. This shift of the S-N-S bending mode toward higher wavenumbers corresponds to an increase in free NTf₂ with increasing temperature and detailed below.

An additional feature of the Raman spectra of ILs containing the NTf₂ anion is the ~740 cm⁻¹ band corresponding to S-N-S bending modes. A blue shift in this ~740cm⁻¹ band (*i.e.* shift toward lower wavenumbers) has been determined to correspond to NTf₂ ions that are less coordinated with the counter cation[433, 440]. Density functional theory calculations show that this peak is actually a combination of two peaks: one that increases in intensity at 748cm⁻¹ corresponding to NTf₂ ions that more coordinated to the cation, and one that conversely increases in intensity at 742cm⁻¹ as the anion becomes less coordinated[438, 443]. This effect is corroborated for the bulk polyIL through observation of a blue shift of this peak with decreasing temperature in the left panel of Figure 101. The narrower width in the M''(ω_c) peak, which is observed following polymerization in nanopores in Figure 97, has been shown to also correlate with increased average ion-to-ion distances in salts[444]. The following qualitatively lists the materials in this study in increasing shift toward more coordinated anions in Figure 100b: 1E3VIm NTf₂ in pores > bulk 1E3VIm NTf₂ > *in-situ* polyIL > bulk 75% polyIL/IL blend > bulk poly1E3VIm NTf₂. Figure 100d shows the ~740cm⁻¹ peak during bulk polymerization over time. Here, the peak maximum does not actually shift, but a more pronounced shoulder at 748cm⁻¹ is observed. Overall, the results in Figures 100 and 101 show that the less coordinated NTf₂ having a higher degree of C1 conformers is favored under confinement.

The ionic conductivity data of the ILs from Figure 98 is now analyzed to determine the fraction of ions that are adsorbed at the silica substrate and make a decreased contribution to long range ion motion. Due to the parallel geometry of the porous silica matrix and the material in the pores, complex impedance (Z^*) can be separated into a linear combination of contributions from the SiO₂ matrix ($Z_{SiO_2}^*$)

and the material inside the pores (Z_{pore}^*). The complex impedance is related to the measured complex dielectric function (ϵ_m^*) through $Z^{*-1} = i\omega\epsilon_m^*C_m$ where C_m is the vacuum capacitance associated with the sample geometry and is the complex dielectric function. Here, $\epsilon_m^* = \epsilon_m' - i\epsilon_m''$, ϵ_m' and ϵ_m'' are the measured real and imaginary parts of the complex dielectric function, respectively. In reports by Iacob *et al.*, the authors used a linear combination of the measured imaginary permittivity to describe dynamics of nanoconfined ILs based on surface area fractions of adsorbed and non-adsorbed ions[353, 445]. We will use a slightly different representation using the real part of the measured complex conductivity, $\sigma'_m = \omega\epsilon_0\epsilon_m''$, to express the dc conductivity values ($\sigma'_m(\omega_c)$) of the 1E3VIm NTf₂ in pores in terms of the contributions from the silica (σ'_{SiO_2}) and contributions from the materials in the pores separated into some layer adsorbed to the pore surface (σ'_a) and some contribution that is bulk-like toward the center of the pore (σ'_b). This is displayed in Eqn. 100 below where the fractions parallel to electrodes for the adsorbed, bulk-like and silica matrix are given by f_a , f_b and f_{SiO_2} , respectively.

$$\sigma'_m = \sigma'_a f_a + \sigma'_b f_b + \sigma'_{SiO_2} f_{SiO_2} \quad 100$$

Even with a porosity of ~7% ($f_b + f_a = 0.07$ and, therefore, $f_{SiO_2} \sim 0.93$), the ion conducting properties of the SiO₂ matrix are so small at measured temperatures and frequencies ($< 10^{-8}$ S cm⁻¹) that the σ'_{SiO_2} term in Eqn. 100 is negligible compared to that of the ions within the pores. Dividing the terms in Eqn. 100 by the bulk conductivity, $\sigma'_b(\omega_c)$, gives us a ratio of the measured conductivity to the conductivity of the bulk fraction ($\sigma'_m/\sigma'_b = f_b$, assuming $\sigma'_a \ll \sigma'_b$). From this we can calculate an estimated fraction of ions that are adsorbed to the pore wall and are inhibited from contributing to the dc conductivity ($F_a = f_a / 0.07$). This fraction of adsorbed ions is displayed in Figure 102, where $F_a \sim 0.55$ ($f_a \sim 0.038$) is constant with temperature. Using this model, Iacob *et al.* found that from 220 K - 250 K the adsorbed surface area fraction of the entire silica membrane with 7.5nm

pores filled with 1-hexyl-3-methyl imidazolium PF₆ increases from $f_a \sim 0.04$ to 0.055 which agrees well with our simple estimation of adsorbed ion fractions[353].

With the ionic radii calculated for NTf₂ (~ 1.85 Å) and 1-ethyl-3-methyl imidazolium (~ 1.5 Å) by Nordness *et al.*, we have sketched a 7.5nm diameter pore filled with 1E3VIm NTf₂ monomer which is displayed roughly to-scale as a schematic inset of Figure 102 with ~ 11 ion pairs spanning the diameter of the pore. The native OH bonds of SiO₂ are known to have a slight negative charge, and, therefore, preferentially interact with the cation[430]. The schematic first displays an adsorbed layer of 1E3VIm cations near the pore surface (in green) closely coordinated with a second layer of anions having the C1 conformer (in orange) that correspond to a larger dipole moment of the NTf₂ anion. This picture is reinforced by results that show that imidazolium cations orient planar to silica surfaces and the SO₂ oxygens of the NTf₂ anion in the *cis* conformation are closely coordinated to the imidazolium ring [433, 446]. From the calculated F_a , a dotted concentric circle which has a radius of 2.5 nm and 0.45 surface area fraction of the 7.5 nm pore cross sectional area is also displayed in the schematic. Within the pore, a count of the cations in the bulk-like layer inside the 5 nm diameter dotted circle constitute $\sim 70\%$ of the cations packed inside the pore. This percentage of adsorbed ions closely resembles the fraction of monomers converted into the polymer backbone (*in-situ* polyIL having $72 \pm 4\%$ conversion of monomers, see Fig. 95b). We expect that these cationic monomers that are effectively immobilized by the electrostatic solvation layer during polymerization remain largely unreacted.

The spatial resolution of the Raman microscope in the X-Y plane is limited to ~ 50 nm and, thus, we cannot experimentally determine changes in anion conformations across a single pore or if the confined cations in the resulting polymer chains are more closely coordinated to the pore walls, the center of the pores or homogeneously distributed within the pore.

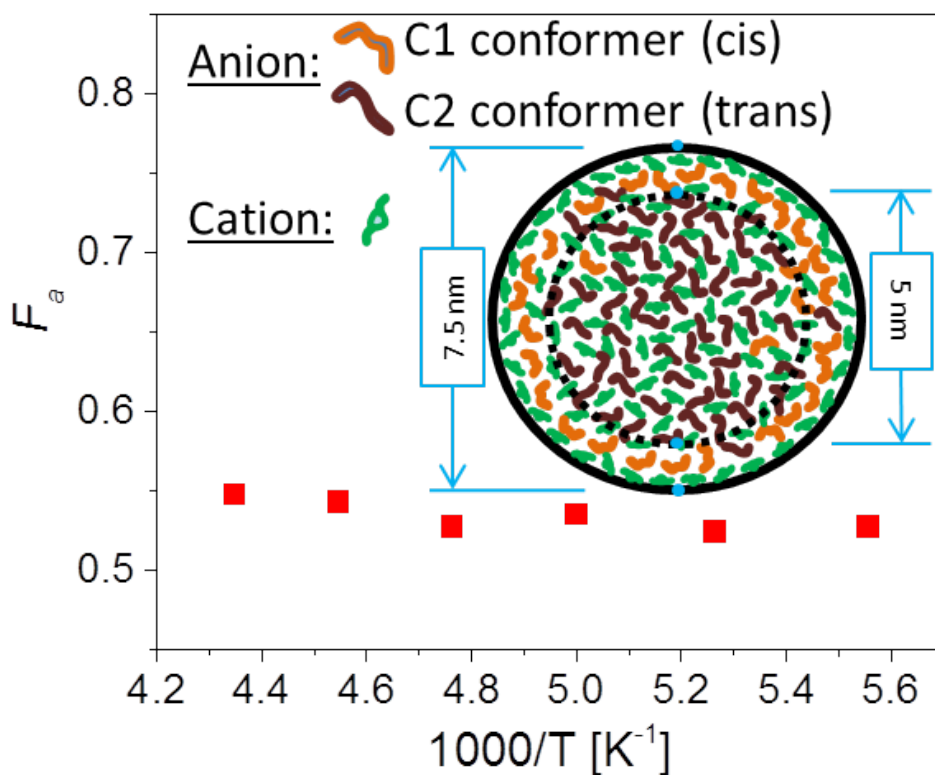


Figure 102: Illustration of the emerging picture of the fraction of ions that are adsorbed to the pore walls (F_a) vs inverse temperature. The inset schematic is a representation of the cross section of a silica nanopore filled with the 1E3VIm NTf₂ monomer. The pore walls are closely associated with cationic monomers which are then surrounded by a layer of anions with the *cis* conformation that exist within this F_a boundary as signified by concentric dotted circle with a 5 nm diameter. C2 conformers are present near the center of the pore and contribute to bulk like ion conduction as shown in Fig. 98.

However, it is evident from the confocal Z-mapping data in Figure 95c and 95d that the pores are uniformly filled with polyIL and IL, which suggests that the polymer chains take on a stretched conformation in the longitudinal direction and is supported by the literature [151].

Using this molecular picture and our results, we expect that the entropic penalty of polymerization in the nanopore is offset by the altered density of the *in-situ* polyIL compared to the 75% polyIL/IL blend as suggested by the NTf₂ conformational equilibrium data in Figure 100. If we consider this penalty in bulk, the entropic cost may be offset by an increased fraction of the larger dipole moment C1 conformer following polymerization, which is similarly observed during crystallization[423, 442]. Additionally, there is a reduced anion-cation coordination of the *in-situ* polyIL compared to the polymer in bulk as shown for the blue shift of the S-N-S bands in Figure 100b. Therefore, as polymerization progresses and reaches a maximum conversion under nanoconfinement, the resulting ion conduction associated with the polymer chains elongated through the pores is higher than the random coiled chains of the bulk polymer as shown in the “confined polymer” conductivity in Figure 98. Additionally, the ion hopping mechanisms of the *in-situ* polyIL are separated into this “confined polymer” portion and a “bulk-like” monomer portion suggesting that the unreacted monomer is no longer adsorbed to the silica surfaces and do not get trapped in the randomly distributed chains as would occur for the 75% polyIL/IL blend even though the chains are diluted compared to the pure bulk polymer.

The molecular picture described above is also in accordance with recent surface force apparatus measurements and simulations that describe electrostatic interactions between negatively charged flat surfaces and imidazolium NTf₂ based ILs that form long-range layer formations from a few ion pairs to ~1 μm [418, 446-448]. Additional evidence from surface force measurements of ILs between flat surfaces predict that at relatively high temperatures, an interplay between electrostatic interactions of silica surfaces and ions cause structural layer

formations at length-scales <10 nm[416, 449]. These layer formations are also described as a liquid-crystalline structured phase, which would likely prefer the crystalline *cis* NTf₂ conformations[441]. Therefore, we conclude that the electrostatic interactions associated with the silica pore walls are experienced by all ions within the pores, but the curvature of the nanopores allows resistance to this radial layer formation. This presumption is qualitatively supported by the dielectric data that exhibit narrower $M''(\omega)$ for the *in-situ* polyIL corresponding to a narrower distribution of ion dynamics times compared to the 1E3VIm NTf₂ in pores.

NTf₂ Conformations for bulk Ammonium-Based PolyIL

For comparison of the NTf₂ conformations described for the 1E3VIm NTf₂ above, Raman spectra were taken for an ammonium-based IL with NTf₂ anion that is often studied in the literature. The monomeric IL was synthesized by quaternization of 2-(dimethylamino)ethyl methacrylate (DMAEMA) with iodoethane in HPLC grade THF solvent. After reaction at 40°C for 24h, excess iodoethane and solvent were evaporated. The resulting 2-(methacryloyloxy)ethyl-dimethylethylammonium iodide was dissolved in miliQ water and LiNTf₂ dissolved in methanol was added dropwise for anion exchange. This mixture was allowed to react for ~4h at 40°C and resulted in an oily phase that separated from the water. This oily phase was decanted and washed several times with miliQ water, and the wash was titrated against AgNO₃ (which forms a AgI precipitate in the presence of iodide) to indicate all iodide was washed from the 2-(methacryloyloxy)ethyl-dimethylethylammonium NTf₂ which was dried for 48h at 60°C. For simplicity, the resulting quaternized IL monomer is termed DMAEMA NTf₂. The AIBN initiator was added to the monomer at 1.3wt% and polymerization was performed in bulk.

The bulk ammonium based PolyIL (polyDMAEMA NTf₂ structure shown in the inset of Fig. 103) was produced and mixed with the monomer at 50 and 75 mol%. The bulk Raman data are shown for several reproduced samples of pure

polymer, pure monomer, 50wt% polymer and 75 wt% polymer at wavenumbers for the NTf₂ anion conformations (see Fig. 103A), for the cation C=C bond vibrations (103B), and for anion coordination (103C). An interesting comparison between the DMAEMA NTf₂ and the 1E3VIm NTf₂ systems is the effect of polymer mol% on the NTf₂ anion conformation. In 103A, no significant change in NTf₂ anion conformation occurs as the ammonium polymer mol% is increased with a relatively high amount of *trans* conformations, which is in contrast to the poly1E3VIm NTf₂. This difference is likely due to imidazolium cation causing the NTf₂ anion to preferentially coordinate on the planar surface of the heterocycle, whereas the spherical ammonium cation has higher degrees of freedom for coordination. Small changes are observed for the NTf₂ ion coordination peak in Figure 103B, but are drastically reduced compared to the imidazolium-based system where the coordination is increased following polymerization (*cf* Fig. 100b). The results in Figures 103A and 103B are confirmed in Figure 103C to be accurate representations of the varied polymer mol% by the reduction in the C=C double bond peaks at ~1640cm⁻¹. This peak is red-shifted compared to the similar peak in the vinylimidazolium monomeric IL (1660cm⁻¹) because of the acrylate monomeric group. The C=O vibrational peak of the ammonium acrylate IL is also shown at ~1730 cm⁻¹ in Figure 103C.

Pores with Surface Modifications

The data and discussion below are the final results collected for this dissertation in March 2020 before the COVID 19 shutdowns. As such, the studies below are not fully complete, and the results are conditional upon measurements that could not be collected for the conversion of the IL monomer to polymer following polymerization in surface modified pores.

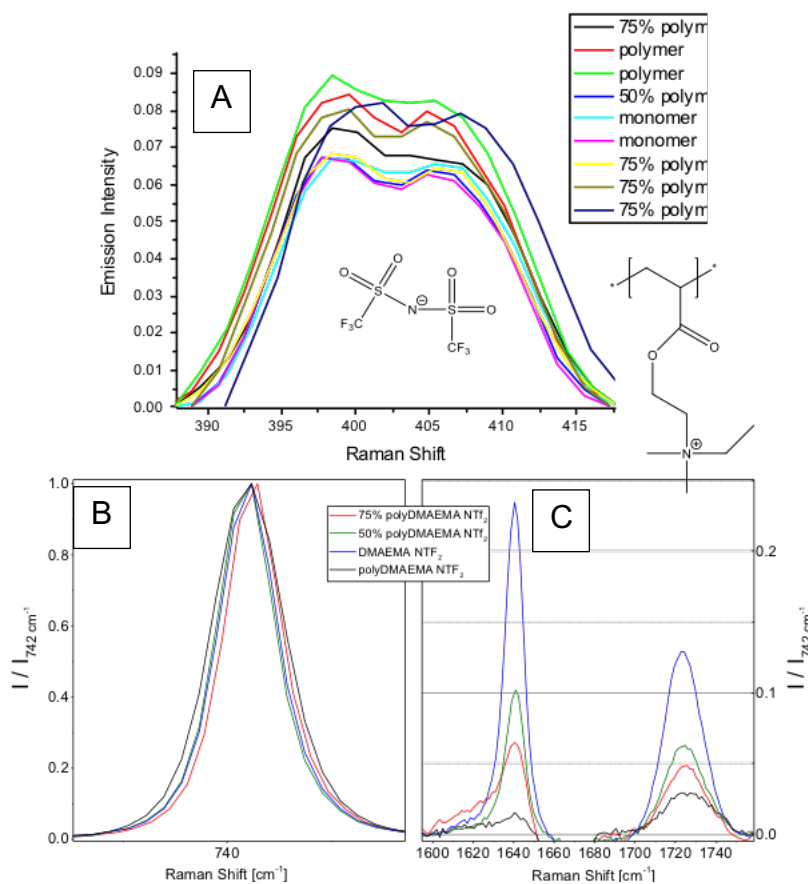


Figure 103: Raman spectra for the bulk state of pure polymer (duplicate samples), pure monomer (duplicate samples), 50mol% polymer (one sample) and 75mol% polymer (quadruplet samples) at wavenumbers for the NTf₂ conformational bands showing relatively high amounts of *trans* conformations (A), at wavenumbers for the NTf₂ coordination with the cation showing few effects by polymerization (B), and at wavenumbers for the C=C bond which reduces at polymer mol% increases (C). The chemical structure in (A) represents the dimethylethylammonium ethoxy methacrylate polymer repeat unit and the NTf₂ *cis* conformer.

Three types of modification of the SiO_2 surface chemistries were accomplished by emerging the membrane in either hexamethyldisilazane (HMDS), (3-aminopropyl)triethoxy silane (APTES), or octyltrimethoxysilane (OTMS) at 80°C for 3h, followed by copious rinsing with ethanol and subsequent drying under ultra-high vacuum at 100°C for 24h. The completion of these chemical surface modifications, Raman spectroscopy was performed for the APTES and OTMS modified pores (see Fig. 104). The HMDS modified pores measured in Figure 104 were the last to be produced and were finished after the Raman lab was shut down for COVID restrictions.

Figure 105 shows the ω_c from M'' curves (top panels) and the σ' value at ω_c (bottom panels) for the 1E3VIm NTf_2 monomer (left panels) and following polymerization (right panels) in the native pores (same data as in Fig. 100) but also including the three chemically modified pores. The conductivity plots (Fig. 105 bottom) have been adjusted for porosity in the same way as before and show that the post-*in situ* polymerization causes a decreased conductivity in the presence of the octyl chains (OTMS) on the pore surfaces. The ω_c rates for all materials post-polymerization are relatively unchanged for the different pore surfaces (Fig. 105 top-right), but for the monomers a similar trend is observed as previously reported (Fig. 105 top left).[358]

Notably, the amine terminated surface modification (APTES) results in an altered temperature dependence for the monomer compared to the other surface modifications (Fig 106 top and bottom left), but this is not observed following polymerization (Fig. 106 top and bottom right). This may be an energetic effect of possible hydrogen bonding between the IL and the APTES surface that increases the activation energy of this process, and following polymerization this energy is overcome by the cations tethered to the polymer backbone and the resulting conformational energy of the chains.

All spectra normalized by area under curve for Si-O-Si bending.
All membranes 50um thick.

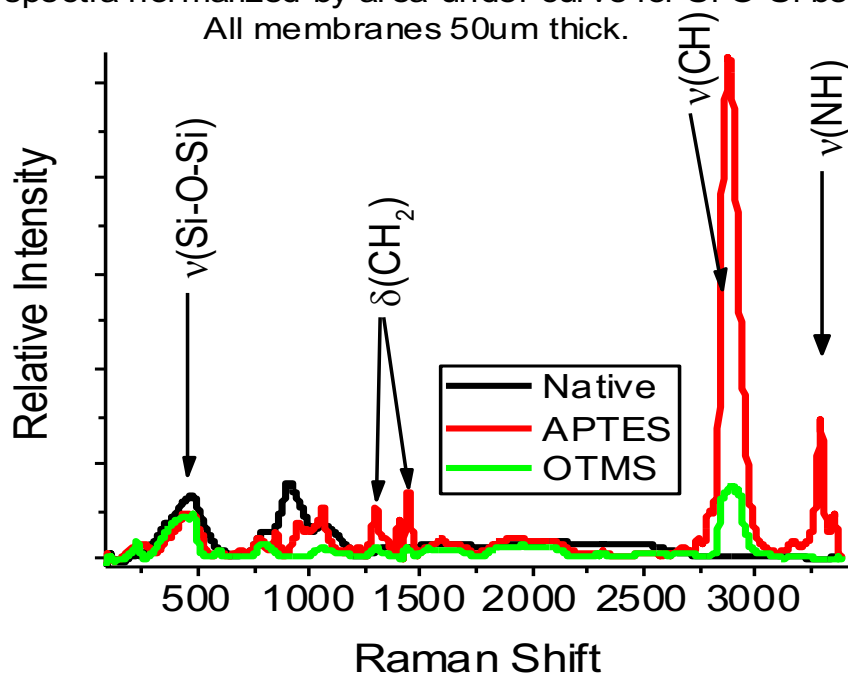


Figure 104: Raman spectra of the native pores and following two chemical surface modifications. The silica bending, CH₂ twisting, CH stretching and NH stretching peaks are identified.

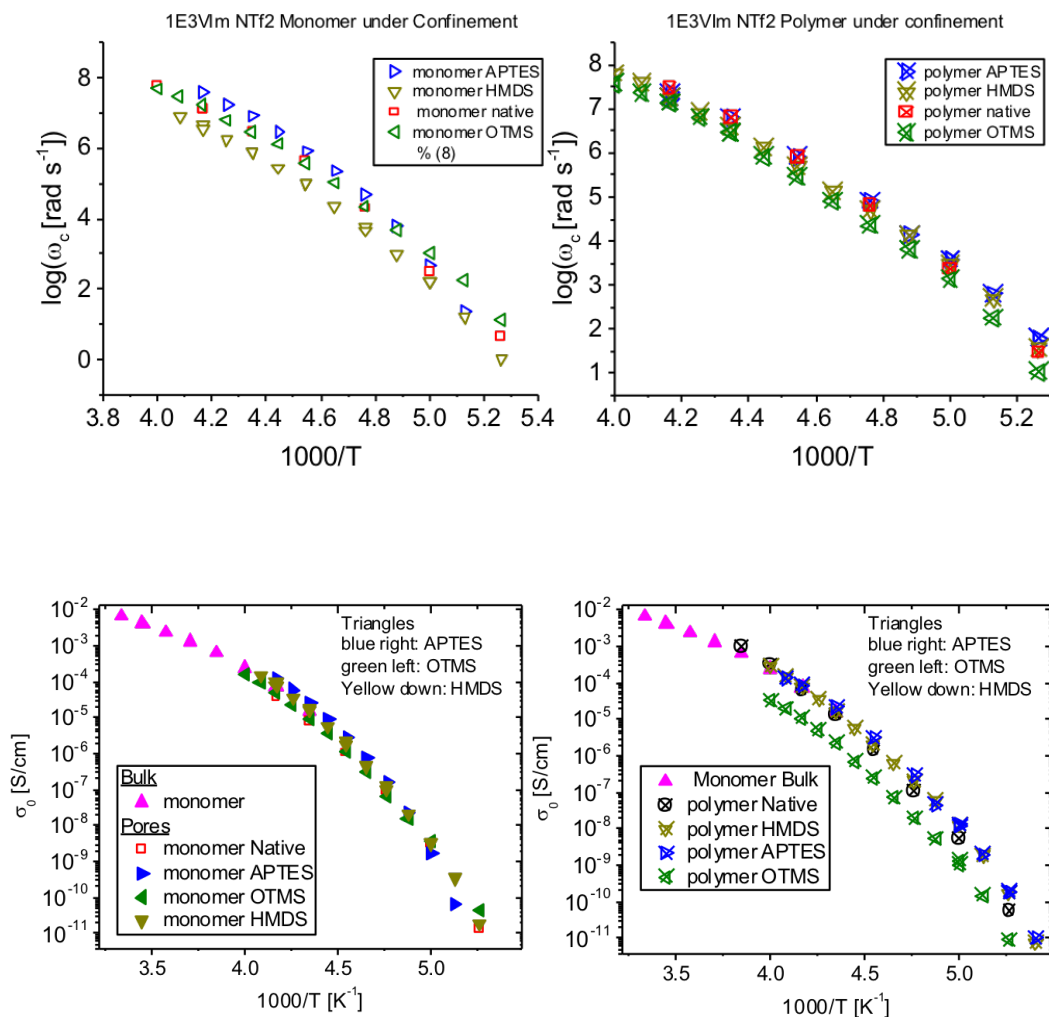


Figure 105: Characteristic ion hopping rate from the M'' peaks (ω_c , top) and the conductivity values at those rates ($\sigma'(\omega_c)$, bottom) for the monomeric 1E3VIm NTf₂ (left) and for *in situ* poly1E3VIm NTf₂ (right) in native and modified pores. The resulting polymerization was not characterized for the material in pores with modified surfaces.

Lastly, Figure 106 compares the rates (Fig 106 left column) and corrected conductivities (Fig. 106 right column) of the 1E3VIm NTf₂ monomer and *in situ* poly1E3VIm NTf₂ for the APTES modification (Fig. 106 top row), HMDS modification (Fig. 106 center row) and OTMS modification (Fig. 106 bottom row). The polymerized IL has higher ω_c at low temperatures for the APTES modified pores (Fig. 106 top left) and at all temperatures for the HMDS (Fig. 106 middle left) compared to the monomer.

The material in the OTMS modified pores shows no change in ω_c following *in situ* polymerization. However, the monomer conductivity is higher for the OTMS pores (Fig. 106 bottom right), compared to the higher conductivities of the polymer at low temperatures for the APTES and HMDS pores. This higher conductivity of the polymer at low temperatures is characteristic of a more Arrhenius like temperature dependence which occurs for the bulk PILs below the T_g . However, these are clearly VFT like dependencies and therefore it is more likely that it is the fragility that is affected under confinement. As mentioned previously, these results do not provide specific conclusions due to the inability to obtain complementary Raman data of monomer or polymer 1E3VIm in modified pores due to Covid-19 lab closures.

Conclusions

In summary, BDS and Raman spectroscopy were employed to investigate ion dynamics, coordination anion/cation pairs and anion conformations in 1E3VIm NTf₂ in bulk and under nanoscale confinement both before and after polymerization. Within the 7.5nm diameter silica nanopores, the polymerization was found to be incomplete resulting in ~75% conversion of the cationic monomers into polymer chains. This is attributed to immobilization of monomeric cations within an adsorbed layer that results from electrostatic interactions with the pore walls.

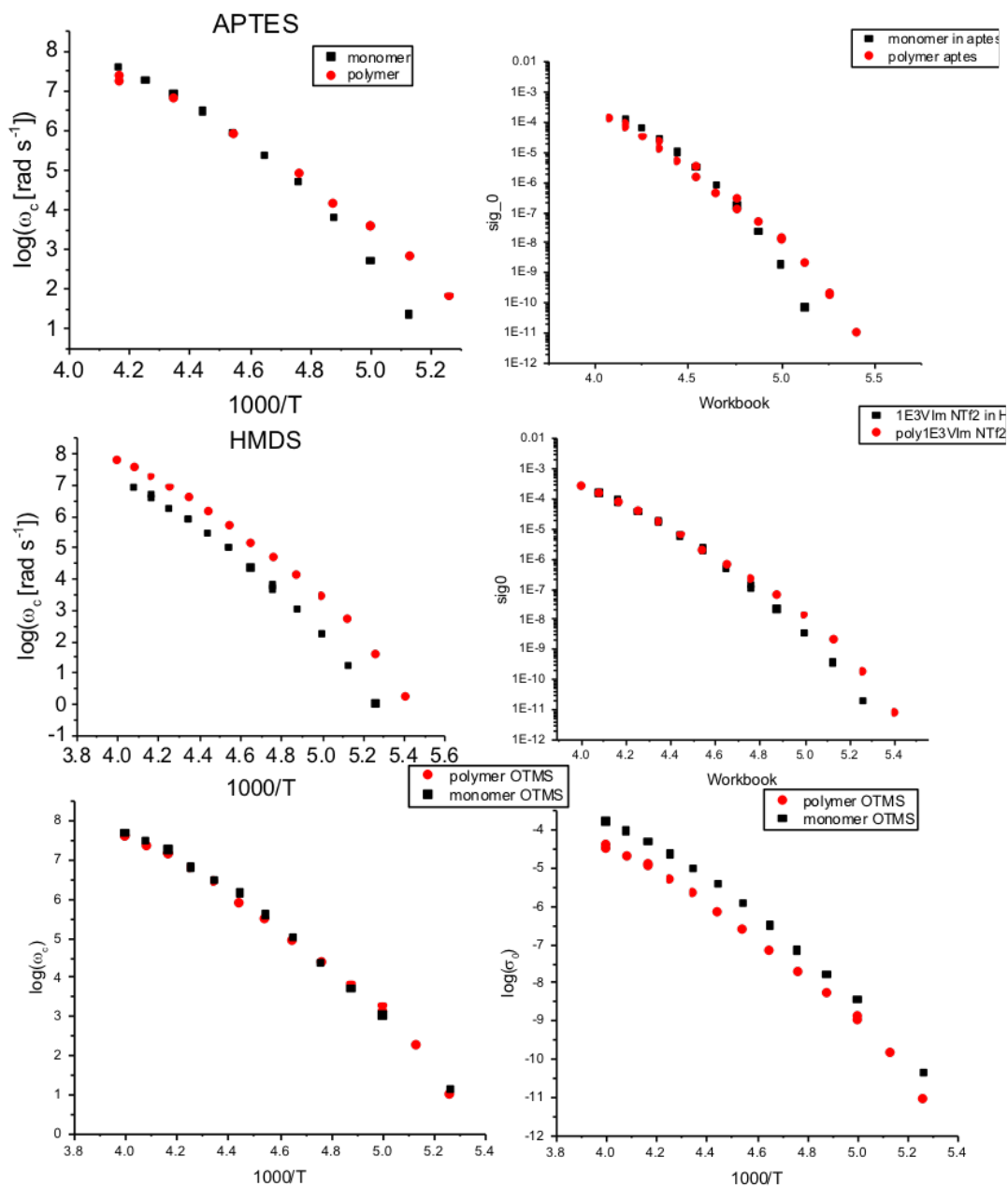


Figure 106: Characteristic ion hopping rate from the M'' peaks (ω_c , left) and the conductivity values at those rates ($\sigma'(\omega_c)$, right) for the monomeric 1E3VIm NTf₂ (black squares) and for *in situ* poly1E3VIm NTf₂ (red circles) in pores with surface modification by APTES (top), HMDS (middle) and OTMS (bottom).

We illustrate this immobilization by showing that ~30% of the cations can pack into a cross sectional pore area exist in a 0.55 surface area fraction as calculated from the ionic conductivities. Two ion dynamics processes are observed for the materials within the pores, whereas only one is observed for the same material in bulk. This suggests that separated phases are present within the pores. An increase in ionic conductivity, $\sigma'(\omega_c)$, is observed for the confined *in-situ* polyIL sample compared to that in the bulk 75 % by weight of a polyIL/IL blend. The Raman bands at $\sim 740\text{ cm}^{-1}$ for the nanoconfined samples is shifted toward lower wavenumbers corresponding to an increase in uncoordinated anions. Additionally, the conformational equilibrium of anion conformers for the *in-situ* polyIL is determined to be the same as that observed in the monomeric IL, while during polymerization in bulk there is an increase in *trans* NTf₂ conformations at roughly 75% monomer conversion. Finally, we determined that for all of the materials measured, those with higher concentrations of NTf₂ C2 conformer correlate to increased ion conduction. These results are useful in a range of applications from those that require knowledge of confined dynamics of ILs and polyILs such as in batteries or supercapacitors to bio-applications such as nanochip anolyte detection and biomimetic transistors.

Part II Conclusions

The role of hard confinement on the dynamics of polymeric systems is a balance between spatial constraints on chain conformation and electrostatic surface interactions between the confined molecules and the confining substrate. In Chapter 7, for the chain dynamics of unentangled polyisoprene (PI) with R_g approaching the size of the pore diameter d (when $d/R_g \sim 2$), the chain relaxation shows characteristics of non-ideal conformations through increased dielectric strength that decreases toward higher temperatures. The relative chain relaxation rates are also shown to change for $d/R_g \sim 2$ where there is a trend of chain relaxation rates becoming more similar to the bulk observed as $d/R_g > 2$ increases. Within the context of other studies on PI chain dynamics in confinement, as the length-scales of the chain and the confinement become similar the effects of electrostatic interactions become less significant compared to the lack of space for the chain to move.

Chapter 8 reveals that the confinement effects are shown to be much different for the polymerized ionic liquid (PIL) compared to PI. When the imidazolium based PIL is synthesized within nanopores, it was determined that the monomer does not reach full conversion into polymer backbone, and is primarily due to electrostatic interactions of the ions with the native Si pore surfaces. However, the ionic conductivity is shown to increase for the PIL prepared under confinement. Raman spectroscopy reveals a conformational shift of the NTf_2 anion at a particular conversion of the monomer that is matched between the synthesis in pores and in bulk. The ammonium-based system on the other hand does not show this anion conformational shift in bulk which suggests that the transport properties of the PIL likely depends on the possible anion-cation association of the planar imidazolium cations compared to the spherical ammonium cation. The effect of pore surface chemistry for transport properties in the imidazolium based PIL (without considering possible conversion of monomer) shows that the alkyl chain chemistry effect is not as great as the alkyl chain length effect. With methyl

and octyl being nonfunctionalized and the propyl being amine terminated, the propyl- and methyl-based surface modifications showed similar dc ionic conductivity and a reduced conductivity for the octyl chemistry. This is disparate to some results from the literature for polymers in modified pores and PILs in larger pores, but in alignment with studies that suggest nanometric confinement can actually increase free volume of the molecular system under investigation [220, 351, 354, 355, 371, 404, 450].

Conclusions and Future Outlook

The dynamics of polymer systems are by their very nature dynamics under confinement. The deviation from random molecular motion for long chain molecules, even when chemical interactions are dismissed, give rise to practical and unique material properties that have been used to build our modern world. Furthermore, as other various types of restrictions are introduced to alter the dynamics of polymers, like phase separated morphologies, molecular architecture, or hard confinement in nanopores, other distinctive properties or enhanced properties have been revealed. The purpose of this dissertation was to progress the fundamental understanding of how these various confinements effect dynamics in order to better develop and design polymeric materials for specific uses. This dissertation presents studies of some heavily considered topics in the past decades combined together to form an aggregate of confinement effects on dynamics beyond those previously recognized for similar systems that ultimately govern the macroscopic properties.

The experimental techniques that are used herein are well developed, powerful tools for probing these dynamics under confinement. With the progress in instrument and measurement science, more sophisticated tools are becoming more widely available to probe these effects more locally and with simultaneous spatial and temporal resolution. Such techniques include AC chip calorimetry for local thermal properties and transitions[451], advanced atomic force microscopy approaches for local perturbations with electric fields, pulse field gradient nuclear magnetic resonance spectroscopy for self-diffusion in block copolymer systems and polymer electrolytes, and neutron scattering methods such as neutron spin echo spectroscopy for matching spatial-temporal relaxations[223]. The use of these types of measurements to probe the fundamental dynamics of polymer systems will advance our ability to control and predict the properties of advanced materials both for confined molecular motion in the bulk state and under nanoscale confinement for composite materials. Further properties that are important to

consider beyond dynamics of the architecturally complex polymers is their optical properties for photonic devices. Additionally, the nonlinear relaxations of block copolymers are considerable for future studies of nonlinear block copolymer architectures[316]. Nanoscale and solid-state ion transport also encompass highly focused fields of study that must also consider surface confinement effects and phase separation on molecular motion. Ultimately, the use of specific structural/spatial/dynamic molecular properties to accurately predict and impose macroscopic properties to a material for its particular use is the fundamental goal of materials science and engineering. Finally, when an understanding of dynamics of the polymer chains or the chain conformations is required, this dissertation and future work in the field of polymer dynamics may be significant contributors to that progress.

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VITA

Thomas started going by Tom just before his fourth year of undergraduate studies during an internship in Bermuda under Dr. Natasha McDonald to collect water column samples in the north Atlantic Ocean to improve satellite imaging and remote sensing of biologically produced chromophores. Growing up near the Gulf of Mexico shaped his love for the coast where he hopes he will eventually return. He is originally from Augusta, GA, but shortly afterward moved to Panama City, FL where he lived until attending high school near Mobile, AL. He remained in Mobile for his post-secondary education at the Jesuit institution of Spring Hill College (SHC) where he studied and received a Bachelor of Science in Chemistry with a minor in Biology in 2013. It was at SHC where Tom met his future wife, Emily King, whom he married in 2018. Just prior to his internship in Bermuda he interned at the Dauphin Island Sea Lab on Dauphin Island, AL under Dr. Ronald Kiene (*Deceased 2019*) to examine the sulfur cycle in salt marshes, estuaries and other biological systems. Upon return from the north Atlantic internship, Tom received a position on Dauphin Island with the Food and Drug Administration's Gulf Coast Seafood Laboratory (GCSL) under Dr. Jessica Jones. At the GCSL, he measured *Vibrio spp.* bacteria levels in oysters and examined the viability of various aquaculture practices to mitigate these levels. Tom and Emily adopted their first dog, Abita, while in Dauphin Island, and after two years they moved to Knoxville, TN for graduate school. Tom joined Joshua Sangoro's research group in the Department of Chemical and Biomolecular Engineering in 2015 and began experimentally studying polymer dynamics. In early 2020, near to his completion of graduate school, the Covid-19 pandemic hit, allowing for him to finish his dissertation remotely with his wife and now two dogs in Boulder, CO, where Emily is working toward her own PhD. He plans to remain in the materials science field, with hopes of eventually working as an experimentalist for a government research agency such as the National Institute for Standards and Technology or a national laboratory.